



# Transition Metal Oxides

*An introduction to their electronic structure and properties*

P. A. Cox

OXFORD

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## An Introduction to their Electronic Structure and Properties

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## PREFACE

Transition metal oxides form a series of compounds with a uniquely wide range of electronic properties. Some of these—the magnetism of lodestone and the colours of gems and minerals containing transition metals—have been known since antiquity. Other properties, especially the ‘high-temperature’ superconductivity of mixed oxides containing copper, have been discovered only recently. Serious attempts to characterize and understand the electronic structure of transition metal oxides began in the late 1930s, but as the discovery of high-temperature superconductors illustrates, these compounds continue to surprise and baffle us in many ways.

The present book is *not* primarily about superconductors, although it is true that the current interest in these compounds provided a strong motivation for writing it. The aim is to describe the range of electronic properties found in transition metal oxides—including magnetic, optical, and spectroscopic properties as well as electrical conductivity—and to discuss in a fairly critical way the various models that have been proposed to interpret them. I have made no attempt at anything approaching a complete survey, which would be quite impossible in such a limited space. Rather, the book is intended as an *introduction* to chemists and physicists who wish to get some idea of what the field is about. I have tried to select both compounds and theories so as to provide a reasonably balanced account, although the choice must inevitably reflect my own interests. Only bulk properties are treated here: surfaces of both transition and non-transition metal oxides will form the subject matter of a forthcoming book in collaboration with Vic Henrich.

The level of the book is intended to be suitable for graduate students and other researchers with a background in solid-state chemistry or physics, or in materials science. Because of this diverse background—which reflects the interdisciplinary nature of the subject—I have included some introductory material. Chapter 1 describes some chemical and structural concepts that may not be familiar to physicists. Chapter 2 explains the different models that have been used to interpret electronic properties; it seems particularly essential to do this, as the theories derive from the very different traditions of physical and chemical thinking about electronic structure. My aim has been to describe the physical basis of the different models, rather than the mathematical details. If theorists are unhappy about the lack of

Hamiltonians and of computational details, then I offer no apologies, as their kind of meat is unfortunately the experimentalists' (and especially the chemists') poison: but they will find references that I hope will provide them with suitable nourishment. In the same way, the discussion of experimental results concentrates on what is being measured, rather than how the experiments are done: again there are plenty of other places where these details can be found.

My interest in transition metal oxides goes back several years, and has been greatly stimulated by collaboration and discussion with many other people in this field. I must mention especially John Goodenough, whose own contributions to this area are paramount, as well as Tony Orchard, Russ Egdell, Andrew Hamnett, Peter Dickens, Tony Cheetham, Marshall Stoneham, and Vic Henrich. The immediate stimulus for this book came from a stay in the United States. In the Fall Semester of 1988 I gave a course of lectures at Cornell University, which formed the basis of the present account. I would like to thank Roald Hoffmann and Frank DiSalvo for the invitation to Cornell, and to many other people there who made my stay so enjoyable. I am also grateful to Vic Henrich and his colleagues for an invitation to Yale, where I tried out some of my ideas, and had many interesting discussions.

A number of people read the first draft of all or part of the book, and I would like to thank especially Marshall Stoneham, Jeremy Kemp, and Wendy Flavell for their helpful and sometimes critical comments. Christine Palmer's assistance in drawing the diagrams was invaluable. Finally, I must thank Christine, Stephen, Andrew, and Emma once again for their encouragement and for their patience during my absences, both physical and mental.

*Oxford*  
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P.A.C.

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## INTRODUCTION

### 1.1 Scope and plan of the book

The three *transition series* form the short groups of elements in the periodic table, interposed between the longer *main groups* (see Fig. 1.1). The occurrence of these elements, as well as the extraordinarily varied chemical and physical properties of their compounds, is a feature of the progressive filling of shells of *d* orbitals across each series.<sup>1,2</sup> The precise boundaries of the transition series vary slightly in different definitions. In oxides, as in other compounds, the properties associated with the *d* shells are most apparent with the elements in the shaded region of Fig. 1.1. All the compounds discussed in this book, therefore, contain an element between Ti and Cu in the *3d* series, between Zr and Ag in the *4d* series, or between Hf and Au in the *5d* series.

Binary oxides contain a metallic element and oxygen, as in  $\text{TiO}_2$ ,  $\text{Fe}_3\text{O}_4$ , or  $\text{NiO}$ . The range of such compounds is already quite large, but it is greatly extended by considering ternary and yet more complex compounds, where additional metallic elements are present. These may themselves be transition elements, as in  $\text{Fe}_2\text{CoO}_4$ , but more frequently in the compounds discussed here the additional elements will be from the pre-transition or post-transition groups, for example in  $\text{LaNiO}_3$  and  $\text{PbTiO}_3$ .

A few transition metal oxides, such as  $\text{OsO}_4$ , are volatile compounds consisting of discrete molecules.<sup>2</sup> By far the majority, however, are solid under normal conditions of temperature and pressure, and it is the properties of these solid compounds which form the main subject of the book. A notable characteristic is the enormous range of electronic properties found.<sup>3</sup> Transition metal oxides may be good insulators ( $\text{TiO}_2$ ), semiconductors ( $\text{Fe}_{0.9}\text{O}$ ), metals ( $\text{ReO}_3$ ), and, of course, superconductors ( $\text{YBa}_2\text{Cu}_3\text{O}_7$ ). Many compounds show transitions from a metallic to a non-metallic state as a function of temperature ( $\text{VO}_2$ ), pressure ( $\text{V}_2\text{O}_3$ ), or composition ( $\text{Na}_x\text{WO}_3$ ). Along with these variations in electrical conductivity go wide differences in other physical properties related to electronic structure. The optical and magnetic behaviour in particular form the basis for many important applications. This range of properties also poses many difficult problems of scientific understanding. The main aim of the book is give examples of the

[illegible]

**FIG. 1.1** The Periodic Table of the Elements. Compounds discussed in this book are oxides containing one or more of the elements shown in the shaded area.

different kinds of electronic properties found in transition metal oxides, and to discuss their interpretation. Applications will be mentioned at appropriate points, although these are not treated in detail.

This chapter is introductory in nature, and discusses some features which form an essential background to the main theme. Chemists have, of course, many important roles to play in studying these materials, not least in the areas of synthesis and characterization.<sup>4-6</sup> It would be inappropriate here to describe the experimental aspects involved. But chemical *thinking* about transition metal oxides, using concepts evolved from studying many different types of compound, is essential for the understanding of electronic properties. Section 1.2.1 describes some chemical concepts that will be used widely throughout the book. It is also important to have some idea of the variables that control the stability of different compounds, and this problem is discussed from the point of view of chemical thermodynamics in Section 1.2.2. The subsequent sections (1.3) describe some of the important features of the crystal structures of transition metal oxides, which are again essential for an understanding of electronic properties. The chapter concludes with an attempt to classify the compounds according to their electronic properties, making use of the chemical classification discussed earlier. Before looking in detail at the different types of behaviour, in Chapters 3 to 5, it is also necessary to appreciate the equally wide range of theoretical models of electronic structure that have been applied to this field. These form the subject of Chapter 2.

## 1.2 Chemical aspects

The following sections introduce, firstly, some of the chemical concepts and language that are essential for thinking about the electronic structure of transition metal oxides and, secondly, some elementary ideas of chemical thermodynamics that are important in understanding the conditions under which these compounds can be studied.

### 1.2.1 Oxidation state and electron configuration

The first step in the chemical characterization of any compound is to establish its precise elemental composition or **stoichiometry**, which is expressed in a chemical formula such as  $\text{TiO}_2$  or  $\text{Na}_{0.7}\text{WO}_3$ . The composition can, in principle, be determined by chemical analysis for the various elements present. Apart from the difficulties and inaccuracies that may be inherent in the analytical procedures, it is important to be aware of various other problems. In the first place, one must be sure

that a polycrystalline sample is a genuinely *single-phase* compound and not a mixture of solid phases with different compositions. Newly prepared samples are usually checked by X-ray powder diffraction; if the desired compound has a simple structure, or one that is known already and listed, for example, in the powder-diffraction file,<sup>7</sup> the X-ray lines should show whether extraneous phases are present. With unknown compounds, especially if their structure is complicated, it is desirable to examine polycrystalline samples by electron microscopy; the analytical facilities available on modern microscopes enable rough compositions of different crystallites to be measured and checked for uniformity.<sup>8</sup>

Even with single crystals, or with polycrystalline samples confirmed as a single phase, problems with composition remain. As the example of  $\text{Na}_{0.7}\text{WO}_3$  shows, many transition metal oxides show the phenomenon of **non-stoichiometry**, where elements are not present in simple integral proportions.<sup>9,10</sup> Variations of stoichiometry are responsible for some of the complexity in structure and properties of oxides. Establishing the precise composition is an essential prerequisite for meaningful interpretations of electronic properties, and can place severe demands on the methods used for synthesis and analysis of these compounds. Within a series with closely related compositions, it is also important to know whether the composition can be varied continuously within a single phase, or whether there is a series of **line phases** each with fixed stoichiometry. The sodium-tungsten bronze series  $\text{Na}_x\text{WO}_3$  shows genuine non-stoichiometry, with  $x$  being a continuous variable up to about 0.9, although there are small structural changes at lower  $x$  values.<sup>11</sup> On the other hand, the molybdenum bronzes  $\text{K}_{0.30}\text{MoO}_3$  and  $\text{K}_{0.33}\text{MoO}_3$  are quite distinct in their structure and electronic properties, and should probably be regarded as compounds with fixed stoichiometry,  $\text{K}_3\text{Mo}_{10}\text{O}_{30}$  for example.<sup>12</sup> Only careful studies, where variation of the preparative conditions is combined with structural and electronic investigations of each composition, can distinguish these two kinds of behaviour.

The oxygen content is a particular problem with many compounds, as this element is normally not analysed for directly, and is easily gained or lost during the course of a synthesis. This quickly became apparent in work on high- $T_c$  superconductors, when it was found that superconducting behaviour is very dependent on the precise preparative conditions, and especially on the environment in which samples were cooled and annealed after synthesis. Thus in the compounds  $\text{YBa}_2\text{Cu}_3\text{O}_x$  compositions with  $x < 6.4$  are non-metallic, whereas superconductivity appears as  $x$  increases towards 7.<sup>13</sup> Again, one must make the distinction between genuine non-stoichiometry and series of line phases with

closely related stoichiometry, as for example in  $W_nO_{3n-1}$  and  $W_nO_{3n-2}$  with integral values of  $n$ .<sup>14</sup> The structural features of this type of line phase will be described briefly later (Section 1.3.3); the distinction between line phases and genuinely non-stoichiometric ones is also discussed from a thermodynamic point of view in Section 1.2.2.

The many disputes which still exist about quite fundamental properties of some oxide systems, such as metallic versus non-metallic properties, or the existence of magnetic moments on transition metal atoms, suggest that different research groups are frequently not studying the same compound, and in particular may have failed to ascertain the oxygen content correctly.

Knowledge of the composition generally leads to an assignment of **oxidation states** to each element present. The chemists' oxidation state is most simply thought of as a formal, or notional, ionic charge.<sup>1</sup> The utility of the *ionic model*, where every atom is imagined to have lost or gained an integral number of electrons, will be explored in Chapter 2. The oxidation-state concept is more general and not restricted to compounds where the ionic model gives a 'good' description. In normal cases, every oxygen atom is assigned a  $-2$  charge, and metal atoms then take up appropriately balancing charges. Thus we have  $Ni^{2+}$  and  $Ti^{4+}$  in  $NiO$  and  $TiO_2$ . In ternary and more complex cases the positive charge must be distributed somehow between more than one element. This causes no difficulty with elements that are known to take only one oxidation state in oxide environments, for example  $Li^+$ ,  $Sr^{2+}$ , and  $La^{3+}$ . It is clear then that  $LiNbO_3$  has  $Nb^{5+}$  and  $LaFeO_3$  has  $Fe^{3+}$ . Ambiguities may arise when charge has to be partitioned between elements, especially transition metals, which show variability in oxidation state. Plausible assignments in ilmenite,  $FeTiO_3$ , could be  $Fe^{3+}$  and  $Ti^{3+}$ , or  $Fe^{2+}$  and  $Ti^{4+}$ . In this case a comparison with the stabilities of oxidation states in aqueous solution (a common oxide environment!) suggests that the latter is more likely, but one might not want to trust such an analogy. It is not evident *a priori* that this kind of distinction is even meaningful. We shall see, however, that different oxidation states of an element do often give rise to characteristically different structural and electronic properties, so that while the concept may have occasional limitations, it is surprisingly powerful in interpreting the electronic structure of a wide range of transition metal oxides. Techniques that have been used to assign oxidation states under different circumstances include structural studies (especially of metal-oxygen distances); magnetic measurements including neutron diffraction and the resonance techniques of ESR and NMR; optical absorption or emission spectroscopy; Mössbauer spectroscopy; and core-level

spectroscopies such as XPS. Their uses (and sometimes abuses) will be referred to later.<sup>15</sup>

Another ambiguity arises in **mixed-valency**<sup>†</sup> compounds, such as  $\text{Fe}_3\text{O}_4$ .<sup>16,17</sup> The average oxidation state is  $\text{Fe}^{2.67+}$ . Does this mean that each iron atom has a fractional oxidation state equal to 2.67, or should one rather think of two  $\text{Fe}^{3+}$  ions to every one  $\text{Fe}^{2+}$ ? Again, only the structure and physical properties can show whether such a distinction is meaningful. In a case such as  $\text{Fe}_3\text{O}_4$ , electrical conductivity is clearly a relevant property. Equal but fractional oxidation states for the iron would imply mobility of electrons between atoms and thus high conductivity. This is in fact found above 120 K, although we shall see that it is more appropriate to think of one  $\text{Fe}^{3+}$  and two  $\text{Fe}^{2.5+}$  rather than three  $\text{Fe}^{2.67+}$  in this case. Below this temperature in  $\text{Fe}_3\text{O}_4$  a transition intervenes (the 'Verwey' transition), in which electrons, and presumably oxidation states, become localized or trapped, so that it is better to imagine integral  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states<sup>19</sup> (see Section 5.3.3).

Mixed valency, in this sense just used for the case of  $\text{Fe}_3\text{O}_4$ , is a very common feature of transition metal oxides, and is often associated with non-stoichiometry. In  $\text{Na}_x\text{WO}_3$  for example, the oxidation state of tungsten is between 5 and 6; as with  $\text{Fe}_3\text{O}_4$  only structural and other measurements can show whether it is reasonable to assign oxidation states to individual atoms. Mixed valency is frequently associated with semiconducting or metallic properties (discussed in Chapters 4 and 5) and appears to be an essential feature of the copper oxide superconductors.<sup>20</sup>

It has been assumed so far that oxygen is to be regarded invariably as  $\text{O}^{2-}$ . This is not always the case. The paramagnetic  $\text{O}^-$  ion has been recognized as a defect in some oxides.<sup>21</sup> Better known as stable species are the peroxide ( $\text{O}_2^{2-}$ ) and superoxide ( $\text{O}_2^-$ ) ions, found in solid salts of alkali metals and in aqueous solution. The O-O distances (148 and 129 pm respectively, compared with 121 pm in  $\text{O}_2$  and at least double this value for the normal distance between oxide ions in crystals) clearly indicate the presence of a bond between oxygen atoms.<sup>2</sup> Peroxide compounds of transition metals are not as common as disulphides containing  $\text{S}_2^{2-}$  (such as  $\text{FeS}_2$ ) but some are known for the earlier transition elements in high oxidation states.<sup>22</sup> For example  $\text{K}_3\text{CrO}_8$  does not contain the improbable  $\text{Cr}^{13+}$ , as its structure shows that Cr is coordinated

<sup>†</sup>The definition of *mixed valency* by chemists is distinct from that which has become common in the physics literature. There it is used to describe compounds such as  $\text{TmSe}$  in which the electronic configuration of Tm apparently fluctuates between two states.<sup>18</sup> The chemical oxidation state of thulium is  $\text{Tm}^{2+}$ , irrespective of this fluctuation. In this book the term 'mixed valency' will be used in its chemical sense of mixed or fractional oxidation state.



by oxygen atoms in pairs, each with an O–O distance of 141 pm characteristic of  $\text{O}_2^{2-}$ ; the more reasonable  $\text{Cr}^{5+}$  is confirmed by the Cr–O distance, and by magnetic measurements which show one unpaired electron per chromium as expected.

Peroxides should be easy to identify if the structure of a compound is well enough known. But there are other situations where it has been claimed that an unconventional assignment of charges represents the electronic structure better. This is the case particularly with ‘high- $T_c$ ’ copper oxide superconductors.<sup>20</sup> The change in composition from  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  to  $\text{YBa}_2\text{Cu}_3\text{O}_7$  suggests the oxidation of some copper from  $\text{Cu}^{2+}$  to  $\text{Cu}^{3+}$ , as the oxidation states  $\text{Ba}^{2+}$  and  $\text{Y}^{3+}$  are essentially invariant. However, many electronic measurements suggest that electrons are being removed from states more closely associated with oxygen than copper atomic orbitals: hence the suggestion that the oxidation should be regarded as a conversion of some  $\text{O}^{2-}$  to  $\text{O}^-$ . This raises the question, not often confronted by chemists who assign oxidation states to elements, of how much these are intended to relate to ‘real’ charges present on atoms in the solid. The problem will be discussed again at the appropriate point (see Section 5.4.2). For the moment, we shall take the conventional chemical view that oxygen is to be regarded as  $\text{O}^{2-}$  unless there is structural evidence for peroxide formation. Although we may often use the ionic model as a first approximation in thinking about electronic structure, we must recognize that a chemical oxidation state is not meant to represent a real ionic charge, but is more of a formal book-keeping device. Of course the reason for using such a concept must lie in its interpretive power, which we shall see through most of the book is impressive; we should not be surprised, however, if such a man-made classification occasionally breaks down and loses some of its utility.

Figure 1.2 shows the range of oxidation states found in oxides containing elements of the three transition series.<sup>2,7</sup> In some cases, marked *T* in the Figures, oxidation states not apparently stable in simple binary oxides can be found in ternary and mixed-valency compounds. Sometimes, an especially high (or low) oxidation state may be of marginal stability, imperfectly characterized, or exist only in a mixed-valency situation. For example  $\text{Fe}^{6+}$  is found in  $\text{BaFeO}_4$ , but this compound probably always has some oxygen deficit, implying the presence of some iron in a lower oxidation state.

The trends apparent in Fig. 1.2 are for the most part characteristic of the elements concerned, and reflected in other aspects of their chemistry. Early elements in each series show progressively higher oxidation states on passing to the right, until a point is reached where high oxidation states become less stable, and the series ends with low ones. The trend