Electronic and optical Properties of d-Band Perovskites

Thomas Wolfram and Sinasi Ellialtioglu



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T. WOLFRAM AND S. ELLİALTIOĞLU Electronic and Optical Properties of *d*-band Perovskites

The perovskite family of oxides includes a vast array of insulators, metals, and semiconductors. Current intense scientific interest stems from the large number of diverse phenomena exhibited by these materials including pseudo-two-dimensional electronic energy bands, high-temperature superconductivity, metal–insulator transitions, piezoelectricity, magnetism, photochromic and catalytic activity.

This book is the first text devoted to a comprehensive theory of the solid-state properties of these fascinating materials. The text includes complete descriptions of the important energy bands, photoemission, and surface states. The chapter on high-temperature superconductors explores the electronic states in typical copper oxide materials. Theoretical results are compared with experimental results and discussed throughout the book.

With problem sets included, this is a unified, logical treatment of fundamental perovskite solid-state properties, which will appeal to graduate students and researchers alike.

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ELECTRONIC AND OPTICAL PROPERTIES OF *D*-BAND PEROVSKITES

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Preface

Metal oxides having the cubic (or nearly cubic), ABO_3 perovskite structure constitute a wide class of compounds that display an amazing variety of interesting properties. The perovskite family encompasses insulators, piezoelectrics, ferroelectrics, metals, semiconductors, magnetic, and superconducting materials. So broad and varied is this class of materials that a comprehensive treatise is virtually impossible and certainly beyond the scope of this introductory text. In this book we treat only those materials that possess electronic states described by energy band theory. However, a chapter is devoted to the quasiparticle-like excitations observed in high-temperature superconducting metal oxides. Although principally dealing with the cubic perovskites, tetragonal distortions and octahedral tilting are discussed in the text. Strong electron correlation theories appropriate for the magnetic properties of the perovskites are not discussed. Discussions of the role of strong electron correlation are frequent in the text, but the development of the many-electron theory crucial for magnetic insulators and high-temperature superconductors is not included.

This book is primarily intended as an introductory textbook. The purpose is to provide the reader with a qualitative understanding of the physics and chemistry that underlies the properties of "*d*-band" perovskites. It employs simple linear combinations of atomic orbitals (LCAO) models to describe perovskite materials that possess energy bands derived primarily from the *d* orbitals of the metal ions and the *p* orbitals of the oxygen ions. The results are usually obtained analytically with relatively simple mathematical tools and are compared with experimental data whenever possible.

The book is considered appropriate for science and electrical engineering graduate students and advanced undergraduate seniors. It may be used as a primary text for short courses or specialized topic seminars or it can serve as an auxiliary text for courses in quantum mechanics, solid-state physics, solid-state chemistry, materials science, or group theory. The reader will need a basic understanding of quantum mechanics, and should have had an introductory course in solid-state physics or solid-state chemistry. Knowledge of group theory is not required, but some understanding of the role of symmetry in quantum mechanics would be helpful. The material covered is considered a prerequisite for understanding the results of more complex models and numerical energy band calculations. Research scientists seeking a qualitative understanding of the electronic and optical properties of the perovskites will also find this book useful.

The theoretical results are derived in sufficient detail to allow a typical reader with a calculus background to reproduce the formulae and derive independent results. Because most of the results are presented in analytic form, the relationships

Preface

among the physical variables are transparent and can easily be understood and explored. Using these analytical results the reader can obtain numerical results for the electronic, optical, and surface properties of specific materials using nothing more sophisticated than a programmable hand calculator or a desk computer equipped with MS QuickBasic[©] software.

Many of the topics discussed in the book were originally published by the authors in research papers and were formulated in terms of Green's functions. In order to keep the material in this book as simple as possible the same results are obtained here by more rudimentary mathematical methods.

For the most part our understanding of the properties of metals is derived from various versions of the free-electron model (often with imposed periodic boundary conditions). The simplicity of this model does not diminish its applicability, and in many instances, particularly in the case of BCS (Bardeen–Cooper–Schrieffer) superconductors, the results obtained are quantitatively correct. Of equal importance is the pedagogical utility of the free-electron model, which permits scientists and students alike to make simple calculations and to develop scientific concepts and a useful intuition about the electronic and optical phenomena of metals.

In the case of compounds whose properties are dominated by the atomic orbitals of the constituent ions, the free-electron model is not particularly useful. For compounds such as the perovskites the physical and chemical properties are largely dependent upon the crystalline structure and the symmetry of the atomic orbitals involved in the valence bands and the bands near the Fermi level. The purpose of this book is to provide a relatively simple but complete description of the *d*-band perovskites based on atomic-like orbitals. Models of this type were developed many years ago by chemists and physicists alike using LCAO and other similar localized-orbital approaches. Later, such models were "put on the shelf" as theoretical solid-state physicists moved almost exclusively into the realm of momentum-space theories. Indeed, for some time it could be said with justification that solid-state physicists were the Fourier transform of solid-state chemists.

With the recent discovery of high-temperature superconductivity (HTSC) in the cuprate compounds interest in the science of the transition metal oxides has grown enormously. Interestingly, solid-state theorists have returned to real-space theories to look for an understanding of these materials. It is somewhat ironic that the original migration to \vec{k} -space was driven, to a large degree, by the success of the BCS theory in explaining (low-temperature) superconductivity in terms of a free-electron model. Now, HTSC is leading solid-state physicists back to realspace approaches. Not withstanding the extreme importance of strong electron correlations, renormalization effects, holons, and spinons, HTSC experimental data are most often discussed in terms of local atomic-like orbitals, the symmetry of the orbitals and the interactions between them. That is, the data are discussed in the jargon characteristic of LCAO models.

Although high-temperature superconductors are not, strictly speaking, perovskites, they share many structural and electronic features in common with the perovskites. For that reason we have included a chapter on the low-lying quasiparticle bands of these exciting, new materials.

Introductory discussion of the perovskites

1.1 Introduction

The mineral CaTiO₃ was discovered in the Ural Mountains by geologist Gustav Rose in 1839 and given the name perovskite in honor of the eminent Russian mineralogist, Count Lev Alexevich von Perovski. The name perovskite is now used to refer to any member of a very large family of compounds that has the formula ABC_3 and for which the *B* ion is surrounded by an octahedron of *C* ions. Perovskites (MgSiO₃ and FeSiO₃) are the most abundant compounds in the Earth's crust.

The compounds with the formula ABO_3 , with O = oxygen and B = a transition metal ion, are a subclass of the transition metal oxides that belong to the perovskite family. Table 1.1 provides a brief list of some well-studied ABO_3 perovskites. Many of the perovskites are cubic or nearly cubic, but they often undergo one or more structural phase transitions, particularly at low temperatures.

The perovskite oxides are extremely interesting because of the enormous variety of solid-state phenomena they exhibit. These materials include insulators, semiconductors, metals, and superconductors. Some have delocalized energy-band states, some have localized electrons, and others display transitions between these

Insulating	Metallic	Magnetic	Superconducting	
			$SrTiO_3(n-type)$	
WO_3	${ m ReO}_3$	$PbCrO_3$	Na_xWO_3 (t)	
$NaTaO_3$	$NaWO_3$	$LaCrO_3$	$K_x WO_3$ (t)	
$SrTiO_3$	$\rm KMoO_3$	$CaMnO_3$	$K_x WO_3$ (h)	
$BaTiO_3$	$\rm SrNbO_3$	$LaMnO_3$	Rb_xWO_3 (h)	
$KTaO_3$	$LaTiO_3$	$LaCoO_3$	Cs_xWO_3 (h)	
$LiNbO_3$	$LaWO_3$	$LaFeO_3$	$\operatorname{Li}_x \operatorname{WO}_3$ (h)	

Table 1.1. Some perovskite and related oxides.

 $t = tetragonal, \qquad h = hexagonal$

two types of behavior. Many of the perovskites are magnetically ordered and a large variety of magnetic structures can be found.

The electronic properties of the perovskites can be altered in a controlled manner by substitution of ions into the A or B sites, or by departures from ideal stoichiometry.

The electronic energy bands of the perovskites are very unusual in that they exhibit two-dimensional behavior that leads to unique structure in properties such as the density of states, Fermi surface, dielectric function, phonon spectra and the photoemission spectra.

The perovskites are also important in numerous technological areas. They are employed in photochromic, electrochromic, and image storage devices. Their ferroelectric and piezoelectric properties are utilized in other device applications including switching, filtering, and surface acoustic wave signal processing.

Many of the perovskites are catalytically active. Development of perovskite catalyst systems for the oxidation of carbon monoxide and hydrocarbons, and the reduction of the oxides of nitrogen have been proposed. The perovskites are also employed in electrochemical applications including the photoelectrolysis of water to produce hydrogen.

Scientific studies of the perovskites date back many years. The physical properties of the tungsten bronzes were investigated as early as 1823 [1]. However, it is only in recent years that experimental and theoretical information on the electronic structure has begun to become available. Energy band calculations [2], neutron diffraction and inelastic scattering data [3], photoemission spectra [4], optical spectra [5], and transport data [6] are now available for materials such as ReO₃, WO₃, NaWO₃, SrTiO₃, BaTiO₃, KMoO₃, KTaO₃, LaMnO₃, LaCoO₃, and a variety of other perovskites.

Surface studies of single-crystal perovskites have been performed using photoelectron spectroscopies that indicate that the surface properties are extremely complex and interesting [7].

In this chapter we present brief discussions of some of the properties of the perovskite oxides. The discussions are qualitative and intended only to give the reader a general impression of the types of factors that must be considered. More quantitative discussions are given in later chapters.

In Section 1.2 we describe the structural features of the perovskites. Sections 1.3 through 1.6 give a qualitative discussion of the electronic states starting from a simple ionic model and then adding ligand field, covalency, and band effects. Section 1.7 deals briefly with localized *d*-electron states and why many perovskites do not have conventional energy bands. In Section 1.8 we touch upon the multiplet config-

urations of localized d electrons and their role in determining the magnetic properties. In Section 1.9 we discuss briefly superconductivity among the perovskites. The last section, 1.10, is a summary of some of the technological applications of the perovskites.

1.2 The perovskite structure

The formula unit for the cubic perovskite oxides is ABO_3 where A and B are metal cations and O indicates an oxygen anion. The structure, illustrated in Fig. 1.1, is simple cubic $(O_h^1, Pm3m)$ with five atoms per unit cell. The lattice constant, 2a, is close to 4 Å for most of the perovskite oxides.



Figure 1.1. The crystal structure of perovskite oxides with ABO_3 formula unit.

The *B* cation is a transition metal ion such as Ti, Ni, Fe, Co, or Mn. It is located at the center of an octahedron of oxygen anions. The *B* site has the full cubic (O_h) point group symmetry. The *A* cation may be a monovalent, divalent, or trivalent metal ion such as K, Na, Li; Sr, Ba, Ca; or La, Pr, Nd. The *A* ion is surrounded by 12 equidistant oxygen ions. The *A* site also has the point group O_h . The oxygen ions are not at sites of cubic point group symmetry. Focusing attention on the oxygen ion marked with an " \times " in Fig. 1.1 it may be seen that the site symmetry is D_{4h}. The *B*–O axis is a fourfold axis of symmetry and there are several reflection planes; the *yz*-plane and planes passing through the edges containing *A* sites. The transition metal ion (*B* site) will experience a cubic ligand field that lifts the fivefold degeneracy of the *d*-orbital energies. The oxygen ions experience an axial ligand field that splits the 2*p*-orbital energies into two groups. These splittings are described in the next section.

Well-known examples of cubic perovskites are $SrTiO_3$, $KTaO_3$, and $BaTiO_3$ (above the ferroelectric transition temperature). Many of the perovskites that we shall want to include in our discussions are slightly distorted from the ideal cubic structure. If the distortions are moderate the general features are not significantly different from those of the cubic materials. $BaTiO_3$ and $SrTiO_3$ both have structural transitions to a tetragonal symmetry at certain critical temperatures. Tetragonal and orthorhombic distortions are very common among the perovskites.

Another class of compounds that we include in our discussions are the pseudoperovskites with the formula unit BO_3 . Such compounds have the perovskite structure except that the A sites are empty. Examples of pseudo-perovskites are ReO_3 and WO_3 .

It is possible to form an intermediate class of perovskites from WO₃ by adding alkali ions to the empty A sites. These compounds, known as the tungsten bronzes, have the formula unit A_x WO₃ where x varies from 0 to 1 and A is H, Li, Na, K, Rb, or Cs. The structure is often dependent upon the value of x. WO₃ is tetragonally distorted but becomes cubic for x > 0.5. NaWO₃ is cubic.

In our discussions we shall also include substituted or mixed compounds of the form $(A_x^1 A_{1-x}^2)(B_y^1 B_{1-y}^2)O_3$ and oxygen-deficient perovskites, ABO_{3-x} . Including distorted, substituted, and non-stoichiometric compounds, the class of materials under consideration is very large. Within this broad class, examples may be found that display almost any solid-state phenomena known.

1.3 Ionic model

The perovskite oxides are highly ionic, but they also possess a significant covalent character. The ionic model is an oversimplified picture but it serves well as a starting point for thinking about the electronic properties. The ionic model assumes that the A and B cations lose electrons to the oxygen anions in sufficient numbers to produce O^{2-} ions. The usual chemical valence is assumed for the A cations; K^+ , Ca^{2+} , and La^{3+} , for example. The ionic state of the transition metal ion is determined by charge neutrality. If the charge of the B ion is denoted by q_B and that of the A ion

Table 1.2. Cations commonly found in perovskite-type oxides. In parentheses is the coordination number, Z, if the radii given are not for 12 coordination; HS and SL refer to high spin and low spin, respectively. The effective ionic radii (in Å) are from Shannon [8].

Dodecahedral A site $(Z = 12)$			Octahedral B site $(Z=6)$		
Ion	Electrons	Radius	Ion	Electrons	Radius
Na ⁺	$2p^{6}$	1.39	Li^+	$1s^2$	0.76
K^+	$3p^6$	1.64	Cu^{2+}	$3d^9$	0.73
Rb^+	$4p^{6}$	1.72	Mg^{2+}	$2p^6$	0.72
Ag^+	$2d^{10}$	1.28(8)	Zn^{2+}	$3d^{10}$	0.74
Ca^{2+}	$3p^6$	1.34	Ti^{3+}	$3d^1$	0.67
Sr^{2+}	$4p^{6}$	1.44	V^{3+}	$3d^2$	0.64
Ba^{2+}	$5p^6$	1.61	Cr^{3+}	$3d^3$	0.615
Pb^{2+}	$6s^2$	1.49	$Mn^{3+}(LS)$	$3d^4$	0.58
La^{3+}	$4d^{10}$	1.36	$Mn^{3+}(HS)$	$3d^4$	0.645
Pr^{3+}	$4f^2$	1.18(8)	$\mathrm{Fe}^{3+}(\mathrm{LS})$	$3d^5$	0.55
Nd^{3+}	$4f^3$	1.27	$\mathrm{Fe}^{3+}(\mathrm{HS})$	$3d^5$	0.645
Bi^{3+}	$6s^2$	1.17(8)	$\rm Co^{3+}(\rm LS)$	$3d^6$	0.5456
Ce^{4+}	$5p^6$	1.14	$\rm Co^{3+}(\rm HS)$	$3d^6$	0.61
Th^{4+}	$6p^6$	1.21	$Ni^{3+}(LS)$	$3d^7$	0.56
			$Ni^{3+}(HS)$	$3d^7$	0.60
			Rh^{3+}	$4d^{6}$	0.665
			Ti^{4+}	$3p^6$	0.605
			Mn^{4+}	$3d^3$	0.53
			Ru^{4+}	$4d^4$	0.62
			Pt^{4+}	$5d^6$	0.625
			Nb^{5+}	$4p^{6}$	0.64
			Ta^{5+}	$5p^6$	0.64
			Mo^{6+}	$4p^{6}$	0.59
			W^{6+}	$5p^6$	0.60

by q_A then $q_B = 6 - q_A$ where the three oxygen ions contribute the factor of 6. A list of the common A ions and their valence states is given in Table 1.2.

Once the charge state of the B ion is determined the number of d electrons remaining is determined from the atomic electronic configuration (Table 1.2). For example, for SrTiO₃ we have Sr²⁺ and O²⁻ so that the titanium ion is Ti⁴⁺. The electronic configuration of neutral titanium atom is [Ar] $3d^24s^2$. To form Ti⁴⁺ the outer four electrons are removed leaving the closed-shell Ar core [Ar]. Since O²⁻ has the [Ne] configuration, all of the ions of $SrTiO_3$ have closed-shell configurations. The electronic configuration of W is [Xe] $5d^46s^2$. Thus in WO₃ the W⁶⁺ ion has a closed-shell [Xe] core; however, for NaWO₃ the W⁵⁺ ion has a d^1 configuration. The electronic configurations of relevant transition metal ions are given in Table 1.2.

According to the ionic model when all of the ions have closed-shell configurations the material is an insulator. If the *B* ion retains *d* electrons then the perovskite may be a metallic conductor depending on other factors to be discussed. NaWO₃ or ReO₃ each have d^1 configurations and are good metals. For compounds such as Na_xWO₃ it is assumed that there will be *x d* electrons per unit cell. That is, the Na donates its electron and the W ions donate the remaining electrons needed to form O²⁻ ions. One may imagine that there are (1 - x) W⁶⁺ and *x* W⁵⁺ ions distributed at random or on an ordered array or that each tungsten ion has an average valence of W^{(6-x)+}. The proper picture can not be decided from the ionic model but depends on other considerations. For Na_xWO₃ experiments show that metallic *d* bands are formed so that we may picture an average valency of (6 - x)+. However, among the perovskites examples of ordered and random arrays of mixed valence *B* ions can also be found.

1.4 Madelung and electrostatic potentials

Starting from the ionic model, other important effects that determine the electronic properties can be added. The ionic model described above would apply to isolated or free ions. The ions are, of course, not isolated but interact in several different ways. One such interaction is through the electrostatic fields due to the charges on the ions. The most important electrostatic effect is the Madelung potential. The A and B ions are surrounded by negatively charged oxygen ions. The electrons orbiting these ions therefore experience repulsive electrostatic (Madelung) potentials. Conversely, the electrons orbiting the oxygen ions are surrounded by positively charged cations and they experience an attractive Madelung potential. The "site Madelung potentials" are defined as the electrostatic potentials at the different lattice sites due to all of the other ions. For example, the Madelung potential at a B site located at \vec{R}_B^0 is

$$V_{\rm M}(\vec{R}_B^0) = \sum_{\vec{R}_{\rm O}} \frac{e^2 |q_{\rm O}|}{|\vec{R}_B^0 - \vec{R}_{\rm O}|} - \sum_{\vec{R}_A} \frac{e^2 |q_A|}{|\vec{R}_B^0 - \vec{R}_A|} - \sum_{\vec{R}_B \neq \vec{R}_B^0} \frac{e^2 |q_B|}{|\vec{R}_B^0 - \vec{R}_B|} \,. \tag{1.1}$$

In (1.1), eq_0 , eq_A , and eq_B are the charges on the oxygen, A, and B ions, respectively, and \vec{R}_0 , \vec{R}_A , and \vec{R}_B are the vectors for the corresponding lattice sites. The site Madelung potentials are very large for the perovskites because of the large ionic charges. Typical Madelung potentials are 30–50 eV for the B site. For

 $A^{2+}B^{4+}O_3^{2-}$ perovskites the (full ionic) site potentials [9] are: $V_{\rm M}(B) = +45.6 \,\mathrm{eV}$, $V_{\rm M}(A) = +19.9 \,\mathrm{eV}$, and $V_{\rm M}(O) = -23.8 \,\mathrm{eV}$. A table of Madelung potentials can be found in Appendix D.

The stability of the perovskite structure is largely due to the energies associated with the Madelung potentials. The attractive potential at the oxygen sites allows the oxygen ions to bind a pair of electrons. In effect the site potential adds to the electron affinity of the oxygen ion. The affinity of O⁻ for the second electron is actually *positive*. This means that the second electron would not be bound on a free oxygen ion. O^{2-} is stable in the lattice because of the attractive site Madelung potential. Conversely, a *d* electron is bound to a Ti⁴⁺ ion with an (ionization) energy of -43 eV. In the absence of the repulsive site Madelung potential, donation of an electron from the Ti³⁺ to an O⁻ ion in SrTiO₃ would be energetically very unfavorable. The site Madelung potential adds to the ionization energy so that the *d* electron would have an effective binding energy of -43 + 45.6 = +2.6 eV (unbound) for SrTiO₃ with the full ionic charges.

Thus, it is seen that the Madelung potentials are responsible for the ionic configurations.

An orbital centered on an ion has a finite radial extent so that an electron in such an orbital would sample the electrostatic field over a distance comparable to the ionic radius. In order to determine the complete effect of the electrostatic field on the electron state we need to know the behavior of the field as a function of position near each ion site. If we use the point ion model then,

$$V(\vec{r}) = -\frac{e^2 |q_B|}{|\vec{r} - \vec{R}_B^0|} + V_{\rm es}(\vec{r}) ,$$

$$V_{\rm es}(\vec{r}) = -\sum_{\vec{R}_B \neq \vec{R}_B^0} \frac{e^2 |q_B|}{|\vec{r} - \vec{R}_B|} - \sum_{\vec{R}_A} \frac{e^2 |q_A|}{|\vec{r} - \vec{R}_A|} + \sum_{\vec{R}_O} \frac{e^2 |q_O|}{|\vec{r} - \vec{R}_O|} .$$
(1.2)

The potential near \vec{R}_B^0 can be found by expanding $V_{\rm es}(\vec{r})$ in terms of spherical harmonics centered at \vec{R}_B^0 . The potential $V_{\rm es}(\vec{r})$ then takes the form of an electric multipole expansion. The monopole term is just the site Madelung potential. Thus, as we have described, the site Madelung potential produces a shift in the energy of an electron localized on the site.

The higher-order multipoles (dipole, quadrupole, etc.) create an electrostatic field (with the point group symmetry of the site) which leads to a lifting of the orbital degeneracies. The effect of the cubic electrostatic field at the *B* ion site is to split the fivefold degenerate *d* states into two groups as shown in Fig. 1.2(c). The e_g group is doubly degenerate corresponding to the *d* orbitals having wavefunctions with angular symmetry $(x^2 - y^2)/r^2$ and $(3z^2 - r^2)/r^2$. The threefold degenerate t_{2g} group corresponds to the states $(xy/r^2), (xz/r^2)$, and (yz/r^2) .



Figure 1.2. Effect of the electrostatic potentials on the ion states: (a) free ions, (b) Madelung potential, and (c) electrostatic splittings.

The oxygen 2p states are split by the axial electrostatic field into a doubly degenerate level denoted by p_{\perp} and a non-degenerate p_{\parallel} state. The notation p_{\perp} and p_{\parallel} refer to 2p orbitals oriented perpendicular and parallel to a *B*–O axis, respectively.

The lowest unoccupied state of the A ion is an s state. Its energy is shifted by the monopole (Madelung potential) but unaffected by the other multipole terms because it is a spatially non-degenerate function with spherical symmetry at a site of cubic symmetry.

The particular level ordering shown in Fig. 1.2 may be understood by considering the orientation of orbitals relative to the charge distributions on neighboring ions. The e_g orbitals have lobes directed along the B–O axis and directly into the negative charge clouds of oxygen ions. The t_{2g} orbitals have lobes pointed perpendicular to the B–O axis between the negative oxygen ions. As a result the e_g states experience a greater repulsion than the t_{2g} states and consequently lie at a higher energy. Similar reasoning suggests that the p_{\parallel} states lie below the p_{\perp} states when it is noted that B ion cores appear as positively charged centers.

In insulating perovskites such as $SrTiO_3$ the p states are completely filled while the d states are completely empty. The energy difference, E_g , between the t_{2g} and p_{\perp} states is approximately equal to the energy gap. Metallic and semiconducting materials have the d states partially filled. NaWO₃ or ReO₃ have a single electron in a t_{2g} state.

In most but not all cases the energy bands involving the s state of the A ion are at energies much higher than the primary valence and conduction bands of a perovskite and therefore these bands are unoccupied. As a result the s state of the A ion usually does not play any significant role in determining the electronic properties. This is not to say that the A ion is not important. The electrostatic potentials of the A ions have a strong influence on the energy of the p-d valence and conduction bands. Furthermore, the size of the A ion is a significant factor in determining whether the crystal structure is distorted from the ideal cubic form. Nevertheless, given a particular perovskite structure and the effective electrostatic potentials acting on the B and O sites, the orbitals of the A ion may usually be omitted from electronic structure calculations. This leads to a major conceptual simplification because the electronic properties of the perovskites may be regarded as arising solely from the BO_3 part of the ABO_3 structure. This implies, for example, that the electronic structure of $BaTiO_3$ and $SrTiO_3$ should be essentially the same. According to the same reasoning the electronic structure of Na_xWO_3 should be independent of x. This does not mean that the properties are the same, but only that the available electronic states are the same. Obviously, the properties of WO_3 are completely different from those of $NaWO_3$; the former is an insulator and the latter is a metal. However, as a first approximation the only effect of the sodium is to donate electrons which occupy the t_{2q} states of the tungsten ion.

1.5 Covalent mixing

In addition to electrostatic interactions, the ions can interact because of the overlap of the electron wavefunctions. This leads to hybridization between the p and dorbitals and the formation of covalent bonds between the transition metal ions and the oxygen ions. It is frequently assumed that the covalent mixing in insulating materials such as $SrTiO_3$ is negligible. This is not correct. Nearly all of the physical and chemical properties of the perovskites are significantly affected by covalency.

To understand covalent mixing we consider a *cluster* of atoms consisting of a transition metal ion and its octahedron of oxygen ions. The wavefunctions of the

cluster can be written in the form:

$$\psi^{(n)}(\vec{r}) = \sum_{\alpha} a^{(n)}_{\alpha} \varphi_{d\alpha}(\vec{r}) + \sum_{\vec{R}_i} \sum_{\beta} b^{(n)}_{i\beta} \varphi_{p\beta}(\vec{r} - \vec{R}_i), \qquad (1.3)$$

where $\psi^{(n)}(\vec{r})$ is the cluster wavefunction for the *n*th eigenstate. $\varphi_{d\alpha}(\vec{r})$ is a *d* orbital on the *B* ion of α -type ($\alpha = xy, xz, \ldots$, etc.) and $\varphi_{p\beta}(\vec{r} - \vec{R}_i)$ is a *p* orbital centered at an oxygen ion located at \vec{R}_i of the β th-type ($\beta = x, y, \text{ or } z$). The coefficients $a_{\alpha}^{(n)}$ and $b_{i\beta}^{(n)}$ are constants which specify the amplitudes of the different orbitals which compose the *n*th eigenstate.



Figure 1.3. Overlap between cation d orbitals and anion p orbitals. (a) Sigma overlap and (b) pi overlap.

For the ionic model the wavefunctions are either pure d orbital $(b_{i\beta}^{(n)} = 0)$ or pure p orbital $(a_{\alpha}^{(n)} = 0)$. For the cluster the wavefunctions are still predominantly d or p orbital in character but there is a significant covalent mixing between the two (both $b_{i\beta}^{(n)}$ and $a_{\alpha}^{(n)} \neq 0$). The mixing comes about because of the overlap between d orbitals centered on the cation and the p orbitals on neighboring oxygen ions. There are two types of p-d overlap. The first is overlap between the d orbitals of the e_g type with p orbitals of the p_{\parallel} type. This overlap is called "sigma" overlap. The second type, "pi" overlap occurs between t_{2g} -type d orbitals and p_{\perp} orbitals. These two types of overlap are illustrated in Fig. 1.3. The overlap between t_{2g} and p_{\parallel} orbitals or between e_g and p_{\perp} orbitals vanishes by symmetry. If only the p and d orbitals are considered then there are 23 cluster states for a transition metal ion and the octahedron of oxygen ions. These 23 cluster states arise from admixtures



Figure 1.4. (a) BO_6 cluster and (b) the cluster levels. The dashed levels are for the electrostatic model. Δ_{es} is the electrostatic splitting.

of the 23 basis states; 5 d orbitals and 18 p orbitals, three on each of the six oxygen ions.

The cluster energy levels [10] are illustrated in Fig. 1.4. The labels given to the cluster energy levels indicate the group theoretical irreducible representations to which the wavefunctions belong. The prefix numbers are used to distinguish different levels which have the same symmetry properties. The degeneracies of the levels are indicated by the numbers in parentheses.

It is noted that the cation d orbitals are still split into the e_g and t_{2g} groups. These, so-called "ligand-field states" differ from those of the electrostatic model (Fig. 1.2) in two significant ways. First, the wavefunctions are no longer just dorbitals. They are admixtures of p and d orbitals. A second difference is that the splitting between the e_g and t_{2g} groups is much larger than for the electrostatic model. The cluster *ligand-field splitting* denoted by 10Dq is due to both electrostatic and covalent effects. The covalent contribution to 10Dq is usually much larger than the electrostatic contribution, $\Delta_{\rm es}$. Typically 10Dq is 2–3 eV in magnitude.

The ligand-field states, $3e_g$ and $2t_{2g}$, have wavefunctions in which the *d* orbitals combine out-of-phase with the *p* orbitals. The interference between the orbitals leads to a *depletion* of charge between the *B* and O ions. For this reason these states are called *antibonding* states. *Bonding* states are formed from in-phase combinations of the *d* and *p* orbitals. These states have wavefunctions that correspond to an accumulation of charge between the *B* and O ions. The bonding states are the $2e_g$ and $1t_{2g}$ levels (shown in Fig. 1.4). These states have hybridized wavefunctions, typically 70% p orbital and 30% d orbital. The percentage d-orbital admixture is a measure of the covalent bonding.

The remaining cluster levels have wavefunctions that are combinations of p orbitals located on the six oxygen ions. They do not hybridize with the d orbitals and therefore they do not contribute to the metal–oxygen bonding. Such states are called *non-bonding* states. Wavefunctions of the three types of cluster states are illustrated in Fig. 1.5.



Figure 1.5. Cluster states: (a) antibonding, (b) bonding, and (c) non-bonding.

It is important to note that electrons occupy d orbitals on the cation even when the $3e_g$ and $2t_{2g}$ levels are unoccupied. This is because of the covalent mixing of the d orbitals into the filled valence states below the $2t_{2g}$ level. This covalency effect is significant even for "ionic" insulators such as SrTiO₃. The ionic model implies that the titanium ion is Ti⁴⁺ with a d^0 configuration. Cluster models would give an effective valence such as Ti³⁺(d^1).

1.6 Energy bands

In the preceding section we considered a cluster model for the perovskites in which the transition metal ion interacts with the nearest-neighbor oxygen ions. The covalent mixing between the cation and anion wavefunctions leads to a partial occupation of d orbitals which, in the ionic model, were empty. A mechanistic interpretation of the covalent mixing is that the overlap between cation and anion wavefunctions provides a means of transferring electrons back and forth between the ions. Clearly, for an extended crystal structure the same mechanism will allow electrons to be shared between cations in adjacent clusters. Each oxygen of a given cluster is shared by adjacent cations. Cations can interact with each other through the intervening oxygen ion. An electron on a cation may be transferred to the oxygen ion and then from the oxygen ion to the second cation. When such processes occur the electrons become delocalized and electron energy bands are formed. It is important to note that the formation of *d*-electron bands requires two independent electron transfer processes. The delocalization of *d* electrons therefore is second order in the p-d overlap (or the probability of p to *d* electron transfer). This is quite different from a typical monatomic metal where delocalization is first order in the atomic overlap. For cubic perovskites the cation–cation separation is nearly 4 Å. This is too large for a significant direct overlap between cation orbitals and therefore band formation occurs by transfer of electrons between cations and anions whose separation is only about 2 Å.

In considering the energy bands of a perovskite it is appropriate to divide the crystal into unit cells each with the formula unit ABO_3 . (The unit cell is shown in Fig. 1.1.) As discussed previously, the *s* states of the *A* ion can be neglected. Therefore, there will be 14 energy bands corresponding to the five *d* orbitals and nine *p* orbitals of each unit cell. The wavefunctions of the band states are characterized by a wavevector \vec{k} and are of the form

$$\Psi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}_d} \sum_{\alpha} a_{\alpha}(\vec{k}) \ e^{i\vec{k}\cdot\vec{R}_d} \ \varphi_{d\alpha}(\vec{r}-\vec{R}_d) + \sum_{\vec{R}_p} \sum_{\beta} b_{\beta}(\vec{k}) \ e^{i\vec{k}\cdot\vec{R}_p} \ \varphi_{p\beta}(\vec{r}-\vec{R}_p).$$
(1.4)

In (1.4), $a_{\alpha}(\vec{k}) e^{i\vec{k}\cdot\vec{R}_d}$ and $b_{\beta}(\vec{k}) e^{i\vec{k}\cdot\vec{R}_p}$ are respectively the amplitudes of the *d* and *p* orbitals of symmetries α and β located at the lattice sites \vec{R}_d and \vec{R}_p .

An energy band diagram for a typical perovskite is shown in Fig. 1.6 for a model which includes only the interactions between nearest-neighbor ions [11]. For this simple model the energy bands divide into a set of sigma bands and a set of pi bands. The sigma bands involve only the $e_g d$ orbitals and the p_{\parallel} oxygen orbitals. The pi bands involve only the $t_{2g} d$ orbitals and the p_{\perp} oxygen orbitals.

The sigma bands have five branches: two distinct σ -type valence (bonding) bands, two distinct σ^* -type conduction (antibonding) bands and a single σ^0 -type non-bonding band. The pi bands have nine branches: three equivalent π -type valence (bonding) bands, three equivalent π^* -type conduction (antibonding) bands, and three equivalent π^0 -type non-bonding bands.

The bonding and antibonding $(\sigma, \sigma^*, \pi, \pi^*)$ bands have wavefunctions whose p-d admixture varies as a function of the wavevector \vec{k} . At $\Gamma(\vec{k}=0)$ in the first Brillouin zone (see the inset in Fig. 1.6) the wavefunctions are pure p or pure d orbital in composition. The states at Γ have no covalent character and therefore correspond to the levels derived from the ionic model including the electrostatic potentials (Fig. 1.2(c)). As \vec{k} varies along $\Gamma \to X \to M \to R$ the covalent mixture of the p and d orbitals increases. It is maximum at the point R, at the corner of the Brillouin zone. The states at R are very similar to the "g" states of the cluster



Figure 1.6. Energy bands for a typical perovskite showing the dispersion for \vec{k} -vectors along various lines in the Brillouin zone (inset) according to the LCAO model with nearest-neighbor interactions. The lighter curves are the pi bands and the darker curves are the sigma bands. The energies, E_g , 10Dq, Δ_d , and Δ_p are the band gap, total (cluster) ligand-field splitting, *d*-orbital ligand-field splitting, and the *p*-orbital ligand-field splitting, respectively.

model (i.e., $2t_{2g}$, $3e_g$, etc.). Thus the ionic model underestimates the covalency and the cluster model overestimates the covalency of the perovskites. The separation between the σ^* and π^* bands at Γ , $\Delta_{\rm es}(d)$, corresponds to the electrostatic contribution to the ligand-field splitting. The separation at R is the total ligand-field band splitting and is approximately equal to 10Dq. The non-bonding band states for σ^0 and π^0 involve only oxygen 2p orbitals and therefore do not involve metal–oxygen covalent mixing. The band and cluster models produce similar non-bonding states.

The energy separation between the π^* and π^0 bands at Γ is the fundamental band gap, E_g . It varies between 1 and 4 eV and is largest for the insulating perovskites. Covalent mixing decreases with increasing band gap. The magnitude of the band gap is a measure of the ionicity of a perovskite. For example, the band gap of SrTiO₃ is 3.25 eV and that of ReO₃ is about 1 eV. This means that SrTiO₃ is much more ionic than ReO₃.

Insulating perovskites (e.g., SrTiO₃, BaTiO₃, or WO₃) have filled valence bands; that is, the σ , π , σ^0 , and π^0 bands are completely occupied with electrons. The conduction bands (σ^* and π^*) are empty. Metallic perovskites such as NaWO₃ or ReO₃ have one electron per unit cell in the π^* conduction band. Examples of metallic compounds with two electrons in the π^* band are CaMoO₃, BaMoO₃, and SrMoO₃. Perovskites with more than two *d* electrons tend to form localized-states similar to those of the cluster model rather than delocalized band states.

Insulating perovskites can be rendered semiconducting or metallic by several means. Reduction in a hydrogen atmosphere produces oxygen vacancies. The vacancies act as donor centers; two electrons being donated by each vacancy (hydrogen itself may also remain in the lattice and act as a donor). Electron concentrations in the range of $10^{16}-10^{20}$ electrons/cm³ can be produced in this way. Reduced insulating perovskites are n-type semiconductors with the Fermi level very near to the bottom of the π^* conduction band. n-type SrTiO₃ has been found to be a superconductor at temperatures below 0.3 K [12].

Insulating perovskites can also be doped by substituting appropriate ions into either the *B* or *A* sites. The tungsten bronzes Na_xWO_3 , K_xWO_3 , Li_xWO_3 , and H_xWO_3 are special cases in which donor ions are substituted into the empty *A* sites of insulating WO₃. Electron concentrations of the order of 10^{22} electrons/cm³ are obtained in this case. Many of the bronze compositions are superconductors.

One of the reasons perovskites are particularly valuable for research is that the electronic properties can be varied in a controlled fashion to produce almost any desired feature. The Fermi level in SrTiO₃ can be varied over a 3 eV range by going from cation- to anion-deficient compositions. The basic band structure does not change appreciably so the properties of such compositions are easily understood and interpreted in terms of a fixed band structure; that is the "rigid-band" approximation is valid. The rigid-band model is also applicable to the tungsten bronzes, and mixed compounds of the $A_x^{(1)}A_{1-x}^{(2)}BO_3$ type where $A^{(1)}$ and $A^{(2)}$ are different cations.

1.7 Localized d electrons

In the preceding section we indicated how the localized cluster states are delocalized because of the overlap of wavefunctions between adjacent clusters. The *d*-band formation is due to the transfer of electrons between cations via intervening oxygen ions. These electrons become delocalized and have an equal probability (proportional to $|e^{i\vec{k}\cdot\vec{R}}|^2=1$) of being found at any cation site. The band model neglects any possible spatial correlation between *d* electrons. The potential experienced by a given electron is assumed to be the same at every lattice site and equal to the average potential of the ion core and all other electrons. The usual one-electron band model explicitly ignores the fact that at any given instant of time a non-average number of electrons may be occupying the orbital of an ion. However, during the lifetime of the "non-average" ionic state the electrons on the site will experience a non-average potential. In particular, the intra-atomic Coulomb repulsion of an electron on a non-average site will be different from that at an average site.

Consider the situation in which we start with two metal ions each having n electrons. The electron–electron repulsion energy among the n electrons at each site is $\frac{1}{2}Un(n-1)$ where U is the Coulomb integral. If we transfer an electron from one site to the other there will be n-1 electrons on one site and n+1 on the other. The electron–electron repulsion energy will be $\frac{1}{2}Un(n+1)$ on the site with the extra electron and $\frac{1}{2}U(n-2)(n-1)$ on the other site. There is a change in the repulsion energy at one site of $\frac{1}{2}U[n(n+1) - n(n-1)] = nU$. At the other site the change in energy is $\frac{1}{2}U[(n-2)(n-1) - n(n-1)] = -Un + U$. Therefore, the net change is an additional repulsive energy equal to U. Thus, there is a Coulomb energy barrier to the creation of non-average ionic states.

Band formation is favorable because the delocalization of an electron reduces its kinetic energy (provided that the electron can occupy a state near the bottom of the band). For such a case the reduction in kinetic energy increases as the band width increases.

It is clear from what has been said that energy band formation will only be favorable if the reduction in kinetic energy is larger than the increase in the Coulomb energy. A variety of models which include a form of the Coulomb correlation energy have been used to find a criterion for the validity of the band model [13]. In general it is found that band theory applies when $W \gtrsim U$ where W is the band width. For W less than U, localized d-electron states are energetically favored. The precise criterion is model-dependent.

The localized electron criterion leads to interesting possibilities for the perovskites. The band width of the σ^* band is substantially larger than that of the π^* band and consequently, for a number of perovskites, the t_{2q} states are localized while the e_g states form σ and σ^* energy bands; LaNiO₃ with filled t_{2g} states and a single electron in the σ^* band is an example [14].

1.8 Magnetism in the perovskites

The occurrence of magnetism in the perovskites is closely connected to the existence of localized d electrons. In almost all cases where magnetism exists the delectrons are localized and possess localized spins. In such cases the local electronic configuration becomes an important consideration. One must be concerned with the multiplet structure. The tendency toward the formation of a multiplet configuration with a net spin arises from intra-atomic exchange and correlation. In atomic theory, Hund's rule states that the lowest-energy configuration corresponds to the state of maximum multiplicity or maximum spin and orbital angular momentum. Hund's rule is qualitatively applicable to the perovskites with localized d electrons. There are, however, some significant differences between atomic theory and the theory applicable to ions of the solid. The major differences between free ions and the cations in a solid perovskite are:

- (1) the fivefold degenerate d states are split into the e_g and t_{2g} groups with a splitting of 10Dq;
- (2) the energy differences between different electronic configurations are not as widely separated as for the free ions;
- (3) there is significant covalent mixing between the d-ion orbitals and the neighboring oxygen ion p orbitals.

As a consequence of (1) and (3) the electronic configuration of the cation should be specified in terms of the one-electron cluster states $3e_g$ and $2t_{2g}$. For simplicity the numerical descriptors of these states may be omitted. The *d*-electron configuration may then be specified by $(t_{2g}^n e_g^m)$, where *n* and *m* are the occupations of the $2t_{2g}$ and $3e_g$ levels, respectively.

The effect of (2) is that different valence states and different electronic configurations of the cation are closer in energy to each other than for the free ion. This is a result of polarization and electron screening of the Coulomb interactions. On applying Hund's rule to a perovskite cation the ligand-field splitting must be taken into account. When the number of d electrons, m+n, is between 4 and 7, Hund's rule can be violated if the ligand-field splitting is greater than the intraatomic exchange energy. Consider, for example, LaMnO₃ which has Mn³⁺ ions with four d electrons. The intra-atomic exchange favors the "high-spin" configuration ${}^{5}E_{g} = (t_{2g} \uparrow^{3} e_{g} \uparrow)$. However, occupying the e_{g} state involves a loss of binding energy equal to the ligand-field splitting. Therefore, the "low-spin" configuration ${}^{3}T_{2g} = (t_{2g} \uparrow^{3} t_{2g} \downarrow)$ is competitive. Assuming a constant exchange, J, between parallel spin electrons, the intra-atomic exchange involves

$$E_{\rm ex} = -J \sum_{i>j} \vec{s}_i \cdot \vec{s}_j,$$

where \vec{s}_i and \vec{s}_j are the spins of the occupied states. The 5E_g has an exchange energy $-\frac{3}{2}J$ while for the ${}^3T_{2g}$, $E_{\text{ex}} = -\frac{3}{4}J$. However, the ${}^3T_{2g}$ has a ligand-field energy of 10Dq. Therefore, the difference in the energies of the two configurations is

$$E({}^{5}E_{g}) - E({}^{3}T_{2g}) = -\frac{3}{4}J + 10Dq \equiv \Delta E.$$

When $\Delta E < 0$ the high spin state ${}^{5}E_{g}$ (spin = 2) is lower in energy than the low spin state ${}^{3}T_{2g}$ (spin = 1). If $\Delta E > 0$ then the low spin state is favored. Experiments on d^{4} ions in perovskites show that the low spin state is usually favored. This indicates that the ligand-field splitting is larger than the intra-atomic exchange and Hund's rule does not apply.

When the cations possess localized spins, then long-range magnetic ordering can occur. The principal mechanism of spin–spin interactions is superexchange. Superexchange involves the antiferromagnetic coupling between nearest-neighbor cations by exchange of electrons with the intervening oxygen ion.

Examples of magnetically ordered perovskites are LaCrO₃, PbCrO₃, CaMnO₃, LaFeO₃, and many others. Those named above form the simple G-type magnetic cell in which the spins of nearest-neighbor cations are antiparallel. Many other types of magnetic ordering also occur among the magnetic perovskites.

As a final comment on localized d electrons we mention the importance of the Jahn–Teller effect. This effect is the spontaneous distortion of a cubic structure such as that of perovskites. When the cation electronic configuration is orbitally degenerate, the ground state will in some cases, be unstable to small distortional displacements. This Jahn–Teller distortion occurs because the electronic energy decreases linearly with displacement while the elastic energy increases as the square of the displacement. A minimum in the total energy always occurs for a small but finite distortional displacement.

1.9 Superconductivity

Superconductivity has been observed for n-type $SrTiO_3$ and for many of the compositions of the tungsten bronzes: Li_xWO_3 , Na_xWO_3 , K_xWO_3 , Rb_xWO_3 , and Cs_xWO_3 . The occurrence of superconductivity in compounds whose elements are not superconducting and for which more than three-fifths of the atoms are oxygen is truly remarkable. WO₃ is an insulator with a tetragonally distorted perovskite structure. With the addition of alkali ions to the empty A site a variety of metallic bronzes can be formed. The tungsten bronzes occur with cubic, hexagonal, and two different tetragonal perovskite-like structures [15]. For Na_xWO₃ the tetragonal I phase occurs in the range 0.2 < x < 0.5. For values of x < 0.2 the tetragonal II phase exists. For values of x > 0.5 the cubic perovskite structure is stable. Tetragonal I, Na_xWO₃ and K_xWO₃ are superconducting with transition temperatures of 0.57 K [16] and 1.98 K [17], respectively. The cubic and tetragonal II phases are apparently not superconducting. Except for Na_xWO₃ and K_xWO₃, superconductivity occurs for the other bronzes when they are in the hexagonal phase [17–19]. The transition temperatures of the hexagonal bronzes are close to 2 K.

It has been found that the transition temperature of the hexagonal bronzes can be raised by a factor of 2 or 3 by etching in various acids [18]. The reasons for this enhancement are not yet clear. The transition temperature of the tetragonal I sodium tungsten bronze, Na_xWO_3 , increases rapidly as x approaches 0.2 [19]. This enhancement occurs as the composition approaches the tetragonal II phase boundary, and is presumed to be associated with a lattice instability.

More recently various alloys of barium bismuthates have been studied extensively. The highest recorded T_c for a non-layered metal oxide is about 30 K for the alloy $Ba_{1-x}K_xBiO_3$ for x = 0.38. This superconducting material displays a transition to an insulating state at x < 0.38, but is a cubic, superconducting metal for 0.38 < x < 0.6. The related compound $BaPb_{1-x}Bi_xO_3$ is also a superconductor with a maximum T_c of about 13 K. $BaBiO_3$ itself is an insulator even though according to conventional band theory it possesses a half-filled conduction band (antibonding Bi 6s-O 2p sigma band).

In 1986 Bednorz and Müller [20] discovered a new class superconducting metal oxides (La₂CuO₄ doped with Ba²⁺, Sr²⁺, or Ca²⁺) one of which possessed a critical temperature, T_c , in excess of 30 K. Their discovery was followed by a worldwide research effort that turned up many other cuprate superconducting materials with even higher critical temperatures, the record high being around 166 K, a temperature that is above the boiling point of liquid nitrogen. These "high- T_c cuprate superconductors" are characterized by sets (one or more layers) of "immediately adjacent" planes of copper ions surrounded by four oxygen ions. Each set of "immediately adjacent" layers is separated from the next set by "isolation layers" (La–O planes in the case of La₂CuO₄) that are poorly conducting. Despite intensive experimental and theoretical research efforts, the mechanisms underlying the high-temperature superconductivity as well as the properties of the "normal" state above T_c are not well understood. However, there seems to be agreement that the two-dimensional character of the Cu–O bonding and the resulting large density of states are important. The question of whether the mechanism of electron pairing