1
Introduction

This first chapter summarizes the main bulk characteristics of insulating oxides, as a prerequisite to the study of surfaces. The foundations of the classical models of cohesion are first recapitulated, and the distinction between charge-transfer oxides and correlated oxides is subsequently established. Restricting ourselves to the first family, which is the subject of this book, we analyse the mixed iono–covalent character of the anion–cation bonding and the peculiarities of the bulk electronic structure. This presentation will allow us to introduce various theoretical and experimental methods – for example, the most common techniques of band structure calculation – as well as some models – the partial charge model, the alternating lattice model – which will be used in the following chapters.

1.1 Classical models of cohesion

Ionic solids are made up of positively and negatively charged ions – the cations and the anions, respectively. The classical models postulate that the outer electronic shells of these ions are either completely filled or empty, so that the charges have integer values: e.g. O^{--} ($2p^6$ configuration) or Mg^{++} ($3s^0$ configuration). The strongest cohesion is obtained when anions and cations are piled up in an alternating way – the anions surrounded by cations and vice versa – , a stacking which minimizes the repulsion between charges of the same sign.

The hard-sphere model

In the first models, due to Born and Madelung, the ions are described as hard spheres, put together in the most compact way (Kittel, 1990).

Ionic radii The radii of these spheres are estimated from inter-atomic equilibrium distances measured in the bulk compounds. Typical values of

the ionic radii are: $r(O^{--}) = 1.4$ Å, $r(Mg^{++}) = 0.78$ Å. They obey some simple rules (van Meerssche and Feneau-Dupont, 1977):

- In a given column of the periodic table, the ionic radii grow with the atomic number: e.g. $r(Li^+) = 0.78$ Å $< r(Na^+) = 0.98$ Å $< r(K^+) = 1.33$ Å.
- For a given element, the ionic radii grow with the electron number: e.g. $r(Fe^{+++}) = 0.67$ Å $< r(Fe^{++}) = 0.82$ Å. This increase is associated with the expansion of the electronic shells induced by electron–electron repulsions.
- Iso-electronic ions have ionic radii which decrease as the atomic number grows, because the electrons are more localized by the attractive field of the nucleus: e.g. $r(O^{--}) = 1.46$ Å $> r(F^-) = 1.33$ Å $> r(Na^+) = 0.98$ Å $> r(Mg^{++}) = 0.78$ Å $> r(Al^{+++}) = 0.57$ Å. In a series of iso-electronic ions, anions are thus larger than cations.

The determinations of ionic radii have been constantly refined. The most recent compilations give values, not only as a function of the charge state of the atom but also as a function of its coordination number Z (Shannon, 1976). An increase in Z is always associated with an increase of the ionic radius: e.g. $r = 0.99$ Å if $Z = 4$, $r = 1.12$ Å if $Z = 7$, $r = 1.24$ Å if $Z = 9$ and $r = 1.39$ Å if $Z = 12$, for Na^+.

Madelung energies The lattice electrostatic energy involves a sum of elementary coulomb interactions between pairs of ions (ij), bearing charges Q_i and Q_j, at a distance R_{ij}:

$$E_M = \frac{1}{2}\sum_{i \neq j} \frac{Q_i Q_j}{R_{ij}} . \tag{1.1.1}$$

This is called the Madelung energy. For a binary crystal containing N formula units, in which the charges are equal to $-Q$ and $+nQ$ (e.g. TiO_2: $Q = 2$, $n = 2$), E_M may be written:

$$E_M = -\frac{NQ^2\alpha}{R} , \tag{1.1.2}$$

as a function of the smallest inter-atomic distance R. The geometric dimensionless constant α, called the Madelung constant, depends only upon the lattice type. Special care must be taken to sum up the alternating series in α. In real space, it is necessary to divide the lattice into neutral entities, without dipolar or quadrupolar moments, according to prescriptions given by Ewald (1921) and Evjen and Frank (Evjen, 1932; Frank, 1950). Summations in reciprocal space may also be performed to reach

convergence more rapidly. Typical values of α are:

NaCl lattice	$\alpha = 1.747565$
CsCl lattice	$\alpha = 1.762675$
ZnS blende lattice	$\alpha = 1.6381$
rutile lattice	$\alpha = 4.816$
β-quartz lattice	$\alpha = 4.439$.

The Madelung energy per formula unit depends upon the lattice type through α, upon the square of the ionic charge and upon the first neighbour inter-atomic distance. For example, E_M/N is equal to 9 eV for NaCl, 48 eV for MgO, and 146 eV for TiO_2 rutile.

Relative stability of crystal lattices The hard-sphere model introduced by Born and Madelung was later used to understand the relative stability of crystal structures. Some structures, typical of binary oxides, are represented in Fig. 1.1. An important parameter is the ratio r_+/r_- between the cation and the anion ionic radii (r_+ and r_-, respectively). When cations

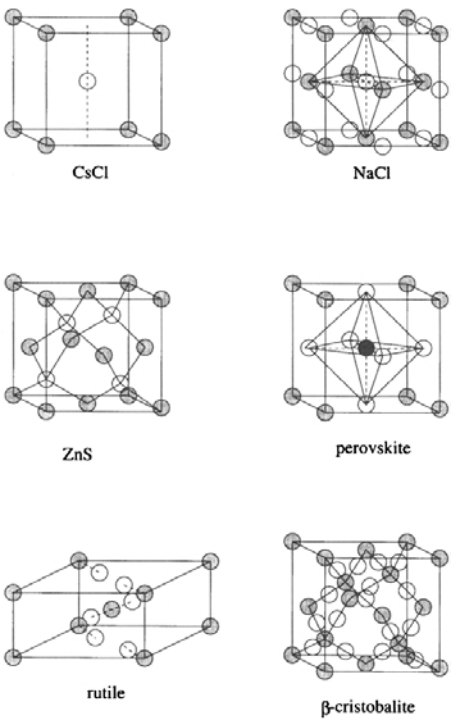

Fig. 1.1 Some binary oxide structures.

are large enough to prevent anion–anion contact, the first neighbour interatomic distance R is fixed by the smallest anion–cation distance and reads $R = r_+ + r_-$. If this is not the case, cations may move in cavities whose size depends only upon the anion radius; then R is fixed by r_-. This regime occurs when r_+/r_- becomes smaller than a critical ratio $(r_+/r_-)_c$, a function of the lattice type. For example, $(r_+/r_-)_c$ is equal to 0.73, 0.41 and 0.22 respectively for the CsCl, NaCl and ZnS structures. The Madelung energy E_M is equal to:

$$E_M = -\frac{NQ^2\alpha}{r_-(1 + r_+/r_-)}, \tag{1.1.3}$$

when r_+/r_- is larger than $(r_+/r_-)_c$, and to:

$$E_M = -\frac{NQ^2\alpha}{r_- [1 + (r_+/r_-)_c]}, \tag{1.1.4}$$

otherwise. The variations of E_M as a function of r_+/r_- are represented in Fig. 1.2 for three simple cubic structures: CsCl (coordination number $Z = 8$), NaCl ($Z = 6$) and ZnS ($Z = 4$). The intersection points of the three curves define the limits of stability for each structure:

ZnS structure	$r_+/r_- < 0.35$
NaCl structure	$0.35 < r_+/r_- < 0.70$
CsCl structure	$0.70 < r_+/r_-$.

Structures with increasing coordination numbers Z correspond to increasing r_+/r_- ratios. The law is qualitatively well obeyed along series of compounds which involve the same anion: for example, in the series LiCl, NaCl, KCl, RbCl and CsCl, the first four compounds display a NaCl structure, while the last one crystallizes in a CsCl structure. In the series NaI, AgI, CsI, along which r_+ increases, a ZnS structure is found for AgI ($r_+/r_- = 0.51$), a NaCl one for NaI ($r_+/r_- = 0.45$) and a CsCl one for CsI ($r_+/r_- = 0.75$). Conclusions qualitatively similar apply to compounds of stoichiometry MX_2 which crystallize in structures such as α-quartz (SiO_2: $Z = 4$), rutile (TiO_2: $Z = 6$) or fluorine (CaF_2: $Z = 8$):

α-quartz structure	$r_+/r_- < 0.41$
rutile structure	$0.41 < r_+/r_- < 0.73$
fluorine structure	$0.73 < r_+/r_-$.

A discussion of lamellar structures and ternary systems may be found in van Meerssche and Feneau-Dupont (1977).

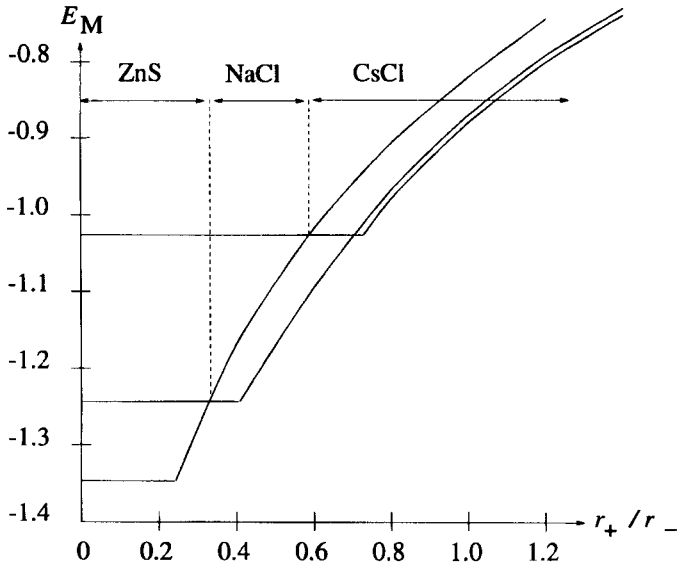

Fig. 1.2. Madelung energy for the three cubic structures ZnS, NaCl and CsCl as a function of the ratio r_+/r_- between the anion and cation ionic radii, at fixed values of r_-. The quantity $-\alpha/(1 + r_+/r_-)$, proportional to E_M, is shown along the vertical axis. The intersection points of the three curves define the limits of stability for each structure.

The iodine series, which was quoted above, proves that the model works well, except in the vicinity of the critical values, where some discrepancies may appear. This shows that the non-coulombic contributions to the cohesive energy, although small in absolute value, may become relevant when tiny energy differences exist. We will discuss the origin of these interactions in Section 1.2.

Pauling's rules The preceding discussion provides an understanding of the four empirical rules which, according to Pauling, control the electrostatic stability of ionic compounds.

- Cations are surrounded by an anion polyhedron. The shortest distance between an anion and a cation is equal to the sum of the ionic radii. The ratio r_+/r_- fixes the coordination.
- The sum of the anion–cation bond strengths, around a given anion, is equal to the charge of this ion. This rule allows a prediction of the anion coordination number in complex structures, such as those met in ternary compounds. It makes use of the concept of bond strength, which, according to Pauling's definition, is equal to the cation charge divided by its coordination number.

- Coordination polyhedra are generally linked by vertices. This is especially true when the cation charge is high and the cation coordination number low. When edges or faces are shared, the structure stability decreases.
- In a crystal with several types of cations, the polyhedra around those which have the higher charge or the lower coordination, tend to avoid each other. This rule is well exemplified in the perovskite structures.

This discussion stresses that, as a first approximation, cohesion is governed by coulomb interactions and that the prediction of equilibrium structures only requires a knowledge of the charges and ionic radii.

Born's model and later developments

The hard-sphere model, presented above in its most simplified form, was later refined in order to account for the cohesion energy and the elastic properties of ionic crystals.

Short-range repulsion A first improvement is related to the repulsive forces which become effective at short inter-ionic distances. In the original model, steric – or hard-core – repulsive forces prevent two ions i and j from coming closer than the sum of their ionic radii r_i and r_j. The short-range repulsion energy is infinite if $R_{ij} < r_i + r_j$, and zero otherwise, which may be written in the form:

$$V_{ij} = \left(\frac{r_i + r_j}{R_{ij}} \right)^n , \tag{1.1.5}$$

with $n = \infty$. The existence of repulsive interactions, impeding inner electronic shells from overlapping, results from Pauli's principle. Yet, there exists no analytical expression deduced from first principles to account for it. Depending upon the fields of research, various empirical laws are used, among which the Lennard–Jones law:

$$V_{ij} = \frac{A}{R_{ij}^n} , \tag{1.1.6}$$

and the Born–Mayer one:

$$V_{ij} = B \exp\left(-\frac{R_{ij}}{\rho} \right) . \tag{1.1.7}$$

Each of these contains two parameters which are functions of the interacting ions i and j: A and n in (1.1.6), with $5 \leq n \leq 12$; B and ρ in (1.1.7), with ρ of the order of 0.2 to 0.3 Å. In both cases, the repulsion energy decreases strongly when the inter-atomic distance gets larger, so that only first neighbour interactions are relevant. The Lennard–Jones form is often

used to describe the cohesion of van der Waals systems, for example rare gas crystals or clusters. In the physics of metals or insulators, one usually chooses the Born–Mayer law, which has a better microscopic basis, since exchange interactions involve atomic wave functions which exponentially decrease far from the nucleus.

Born's model, or rigid-ion model In Born's model, the total energy of a binary compound, containing N formula units, is thus equal to the sum of the Madelung energy E_M and the short-range repulsion energy between first neighbours (Born and Huang, 1954; Tosi, 1964):

$$E = -\frac{NQ^2\alpha}{R} + NZB\exp\left(-\frac{R}{\rho}\right) . \tag{1.1.8}$$

The crystal structure determines the Madelung constant α and the number Z of anion–cation bonds per formula unit. In binary compounds, Z is equal to the coordination number of the ion which has the larger number of first neighbours (e.g. $Z = 6$ for TiO_2). The minimization of E with respect to R yields the equilibrium distance R_0 between first neighbours in a given structure. R_0 is the solution of the implicit equation:

$$ZB\exp\left(-\frac{R_0}{\rho}\right) = \frac{\rho\alpha Q^2}{R_0^2} . \tag{1.1.9}$$

The cohesion energy, necessary to separate the system into independent ions, is equal to:

$$E_{coh} = N\frac{\alpha Q^2}{R_0}\left(1 - \frac{\rho}{R_0}\right) . \tag{1.1.10}$$

The first factor in the parenthesis is associated with E_M and the second with the short-range interactions. Since the ratio between ρ and R_0 is generally of the order of 0.1, the largest contribution to the cohesion energy is E_M, which justifies *a posteriori* the hard-sphere model. Despite its simplicity, Born's model has been used with success in many different instances; for example, it has helped in the interpretation of many bulk phonon dispersion curves (Bilz and Kress, 1979).

Improvements Further improvements have been introduced, as experimental data have become more reliable. For example, neutron scattering experiments have proved that the longitudinal optic mode frequencies at the zone centre are systematically lower than predicted. Various models result from the idea that this discrepancy may be assigned to the neglect of ionic polarization.

- The shell model: the ions are described by a core, including the nucleus and the inner electrons, and a zero-mass shell representing the valence electrons (Dick and Overhauser, 1958). The core and the shell bear opposite charges. They are harmonically coupled by a spring of stiffness k. The electric field $\mathscr{E}$ exerted by neighbouring ions shifts the shell with respect to the core position. If Y is the shell charge, $\mathscr{E}$ induces a dipole moment equal to $\mathscr{E}Y^2/k$. The ion polarizability α' in the model, is thus equal to: $\alpha' = Y^2/k$. The value of k may be deduced from the value of the optical dielectric constant ϵ_∞ thanks to the Clausius–Mosotti relationship:

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi\alpha'}{3} \,. \tag{1.1.11}$$

  Only short-range inter-ionic forces between the shells are taken into account, while long-range forces involve all species, except the core and shell associated with the same ion. The weak polarizability of the cations is very often neglected.
- Other refinements: in the literature, many other refinements to Born's model have been introduced: among others, one finds models which take into account the mutual ion polarizability (van der Waals interactions), the extended shell model, the overlap shell model, the deformable shell model, the breathing shell model and the double shell model (Cochran, 1971). In covalent crystals such as diamond, where the charges are not located on the sites but rather on the bonds, the so-called bond charge model was proposed. Some authors found it necessary to introduce non-integer charges in some systems: in a classical approach, this raises the question of potential transferability and of the nature of the quantum terms responsible for the charge transfers. During the last few years, an increasing effort has been put on the derivation of inter-ionic potentials from *ab initio* methods (e.g. Allan *et al.*, 1990; Harding, 1991; Harrison and Leslie, 1992; Purton *et al.*, 1993; Allan and Mackrodt, 1994). The classical models are generally recognized to be less well suited to open shell systems, like transition metal oxides, than to simple oxides (Stoneham and Harding, 1986). More details on all these models may be found in specialized papers on this subject (Bilz and Kress, 1979). In most cases, it is likely that the increasing complexity of classical models simply hides the need to treat the quantum effects correctly.

Applications of the atomistic models

The pair potentials have been widely used to describe various cohesion properties of insulating compounds:

- bulk static properties, such as the cohesion energy, the thermal expansion coefficient, the relative stability of polymorphs (Catlow and Mackrodt, 1982),
- structural phase transitions, such as the anti-ferrodisplacive cubic–tetragonal transition in $SrTiO_3$, the tetragonal–orthorhombic transition in La_2CuO_4 (Piveteau and Noguera, 1991) or the amorphization of α-quartz under pressure (Binggeli *et al.*, 1994),
- bulk dynamic properties: the phonon dispersion curves, the bulk modulus and the elastic coefficients (Bilz and Kress, 1979),
- thermodynamics of defects: the energies of formation of defects, the vacancy migration energy (Harding, 1990), the thermodynamics of non-stoichiometric oxides (Harding, 1991; Boureau and Tetot, 1989), the simulation of superionic conductors (Lindan and Gillan, 1994),
- surface static properties: the surface tension, the relaxation effects (Catlow and Mackrodt, 1982; Mackrodt, 1988),
- surface dynamic properties: the phonon frequencies, the vibrational entropy, the mean square displacements (Kress and de Wette, 1991),
- surface defects: steps, kinks, doping, surface vacancies (Mackrodt, 1984; Stoneham and Tasker, 1988; Colbourn, 1992),
- interfacial properties (Stoneham and Tasker, 1988),
- small cluster properties (Martins, 1983; Ziemann and Castelman, 1991).

1.2 Origin of the insulating state

While the classical models can reproduce and sometimes predict some structural properties, they are unable to inform about the electronic characteristics of insulators, because they assume that the electrons are frozen around the ionic cores. The next step consists in finding the microscopic origin of the forbidden gap present in the electronic excitation spectrum, which is the defining property of the insulating state.

Charge-transfer oxides; correlated oxides

The gap width is fixed by the electronic excitation of lowest energy. Starting from a classical model with localized electrons, two types of excitations may be considered.

Charge-transfer excitation When an electron is transferred from an anion to a cation, a charge-transfer excitation is produced:

$$X^{n+} + O^{--} \rightarrow X^{(n-1)+} + O^{-} . \qquad (1.2.1)$$

The charge-transfer energy Δ is related to the cation nth ionization potential I_n and to the oxygen second electronic affinity A_2. To a first

approximation, Δ reads:

$$\Delta = A_2 - I_n - V_X + V_O \,, \tag{1.2.2}$$

if the two ions are infinitely far from each other, or:

$$\Delta = A_2 - I_n - V_X + V_O - \frac{1}{R} \,, \tag{1.2.3}$$

if they are located at a distance R; in these expressions, V_X and V_O are the electrostatic potentials acting on a cation ($V_X < 0$), and on an oxygen anion ($V_O > 0$). For MgO, in which $A_2 = -9$ eV, $I_2 = 15$ eV, $V_O = -V_X = 24$ eV and $R = 2.1$ Å, $\Delta = 17$ eV, while for NaCl, $\Delta = 11.5$ eV ($A_1 = 3.76 \pm 2$ eV, $I_1 = 5.14$ eV, $V_O = -V_X = 8.9$ eV and $R = 2.82$ Å). For NiO: $A_2 = -9$ eV, $I_2 = 18.15$ eV, $V_O = -V_X = 24.1$ eV and $R = 2.09$ Å, which yields $\Delta = 14$ eV. The values found for Δ, in this simple approximation, are larger than the measured gap widths, which are respectively equal to 7.8 eV, 8.9 eV and 4 eV for the three compounds.

Cation charge fluctuation A second type of excitation may occur when two cations exchange an electron. Its energy U is associated with the reaction:

$$X^{n+} + X^{n+} \rightarrow X^{(n-1)+} + X^{(n+1)+} \,. \tag{1.2.4}$$

It is related to the $(n+1)$th and nth cation ionization potentials I_{n+1} and I_n, corrected by an electrostatic term; U reads, to a first approximation:

$$U = I_{n+1} - I_n - \frac{1}{R} \,. \tag{1.2.5}$$

This approach yields U close to 13 eV in NiO ($I_3 = 36.16$ eV, $I_2 = 18.2$ eV and $R = 2.96$ Å), a value slightly lower than the charge-transfer excitation energy. The cation charge fluctuations have to be considered whenever the ions have an unfilled outer electronic shell. Otherwise, the energy difference $I_{n+1} - I_n$ is very large and cannot be the lowest excitation energy of the system.

In a compound, when U happens to be large, the electronic structure can no longer be described by a one-electron effective Hamiltonian, and the mean-field approaches for electron–electron interactions are not valid. In a mean-field approximation, all the electronic configurations on a given ion have equal probabilities. For example, the two-electron wave function of the hydrogen diatomic molecule involves the configurations H–H and H^+H^- with equal weight, in the bonding state. Beyond the mean-field approximation, the configuration H^+H^- has a decreasing weight as U gets larger: the electrons move in a correlated way to avoid being located on the same atom. A partial localization results, which the band structure calculations do not reproduce well (Mott, 1974). In the physics of