



**UNIVERSITY
OF OSLO**

Defects and Transport in Crystalline Solids

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1. Bonding, structure, and defects

Preface

In 1972 Per Kofstad published his "Non-stoichiometry, diffusion and electrical conductivity in binary metal oxides". It has been a popular textbook in defect chemistry of oxides worldwide, not least because it contained a comprehensive review of defect structure and defect-related properties of all binary metal oxides. It followed Kofstad's equally well-recognized book "High temperature oxidation of metals" from 1966, later revised and published under the title "High temperature corrosion" in 1988.

In the quarter of a century that has passed since 1972 the field of defect chemistry in oxides has grown and developed in many ways. New and improved measurement techniques, new synthesis techniques, as well as skilled and devoted investigators have produced better data for many oxides, partly encouraged by industrial developments in the use of solid electrolytes (solid oxide fuel cells, gas separation membranes, ceramic electrodes, catalysts, etc). Computer modelling enables detailed analysis of defect chemistry and transport processes, and helps us interpret experimental data. Although the increasing accuracy and complexity is welcome and unavoidable, the sound overview and ability to analyse a situation may be obscured or lost. The newcomer may find the field difficult to enter.

Along with the developments of theory and modelling, the field has changed focus from binary oxides to ternary or higher oxides. This is much due to the growing awareness that perovskites and related structures tolerate very large substitutions and variations in valence and stoichiometry. They display a wide variety of properties and applications. Here we find lanthanum aluminate insulators, titanate and zirconate electroceramics with ferroelectricity, piezoelectricity, etc, the high- T_c cuprate and other superconductors, high-temperature electronic conductors such as doped lanthanum cobaltate and chromite, high temperature ionic conductors such as doped lanthanum gallate, mixed conductors, and alkaline earth cerates which dissolve protons and become proton conductors at high temperatures.

A revision of the book from 1972 as such is thus utopic in many respects. In the early 1990s Kofstad decided to author a new text that represented a development of the general and theoretical first part of the former book, while he intended to include only a few examples of data from important example oxide systems. After having sketched the book he was struck by cancer in 1993. He fought the cancer for four years, with the obligation to finish the book as one of the driving forces. However, deprived of much of his usual strength, he was unable to finish the work. I became engaged as a co-author at that time with the purpose of completing the book.

I used the new text as a curriculum when I took over the teaching of Kofstad's course in defect chemistry at the University of Oslo, thereby being able to adjust and hopefully improve it step by step. However, the book has not been finished or published. Another textbook on defect chemistry by Kofstad's close friend and colleague, Donald M. Smyth was published and took away some of the immediate need for our textbook. All in all I have felt that the new book needs more work and refinement. With the present text I am still in the middle of that process, and feedback is thus as welcome as ever.

Truls Norby, September 2010

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1. Bonding, structure, and defects

In this chapter we will first briefly introduce defects in elemental and ionic solids, so that we have an idea what we are heading for.

Next we will go through some themes familiar to those who have a background in inorganic and solid state chemistry and physics or materials science; bonding, periodic properties of the elements, electron energy bands of solids, and packing and structures. This is meant as optional reading for repetition or those new to these fields.

We then arrive at the important lesson: Introduction of a terminology and notation for structural elements and defects, especially charged defects. By learning the terminology and notation for defects, we expect to obtain also at a reasonable first overview of types and constitution of simple defects. We will furthermore learn how to set up the electroneutrality condition for systems with effectively charged defects.

We then learn some simple defect pairs related to disorder and non-stoichiometry. We round off by looking briefly at more complex defects, much because the remaining course will return and stay with the simple defects on which we can apply equilibrium thermodynamics and transport theory.

Introduction

During the 19th century crystallographers concluded that the atoms or structural units in crystals were arranged in ideal structures where all the structural sites were occupied. Chemists, on their side, expressed the compositions in terms of the law of definite proportions and generally believed that inorganic compounds had definite, unvarying, stoichiometric compositions determined by the valence of the constituent atoms. However, there was still considerable discussion regarding these concepts and it was alternatively proposed that inorganic compounds can have variable compositions. This was clearly established in the beginning of the 20th century and the question was theoretically resolved in the 1930's when Wagner and Schottky (1930) showed through statistical thermodynamic treatments of mixed phases that crystal structures are not ideal. Some structural sites will be empty (vacant) and extra atoms may occupy the interstitial space between the atoms on the structural sites. The empty structural sites are termed vacancies and the extra atoms interstitial atoms. Following Wagner and Schottky all crystalline solids will at any temperature above 0 K contain vacancies and extra atoms and will as such exhibit deviations from the ideal structure. Furthermore, all inorganic compounds may in principle have variable composition and thus be nonstoichiometric. In fact, the very exact stoichiometric composition is an exception rather than a rule and can under equilibrium conditions only be achieved at definite sets of temperature and activities of the components in a crystal. However, for many inorganic compounds the deviation from stoichiometry (the nonstoichiometry) is so small that it is difficult or impossible to measure it directly with presently available experimental techniques.

These deviations from the ideal structures are present at any temperature and occur naturally in all crystalline compounds. Even so these deviations or imperfections are called *defects*. The reason for this is that by convention the *ideal structure* is used as the reference state, and any deviation from this ideal state is termed a *defect*.

Crystalline solids contain different types of structural defects. If the imperfection is limited to one structural or lattice site and its immediate vicinity, it is a zero-dimensional imperfection and is termed a *point defect*. Vacancies and interstitial atoms are point defects. An impurity atom present in a crystal and that either occupies a structural site or an interstitial site is also termed a point defect. But in addition to the point defects the structural defects also comprise line and plane defects. The *line defects* or 1-dimensional defects comprise *dislocations*, which are characterised by displacements in the structure in certain directions. The *plane defects* or 2-dimensional defects comprise *stacking faults*, *grain boundaries*, *internal interfaces* and *external surfaces*.

Figure 1-1 shows a schematical representation of some defects in an elemental solid, e.g. a metal like Ni or a semiconductor like Si. The vacancy, interstitial foreign atom, and substitutional atom are zero-dimensional point defects. The dislocation – when assumed continuing by repetition into the plane of the paper – is a one-dimensional defect. The same goes for the line of vacancies that runs only in the plane of the paper. The precipitation – if considered to have an extension into the plane of the paper – is a three-dimensional defect.

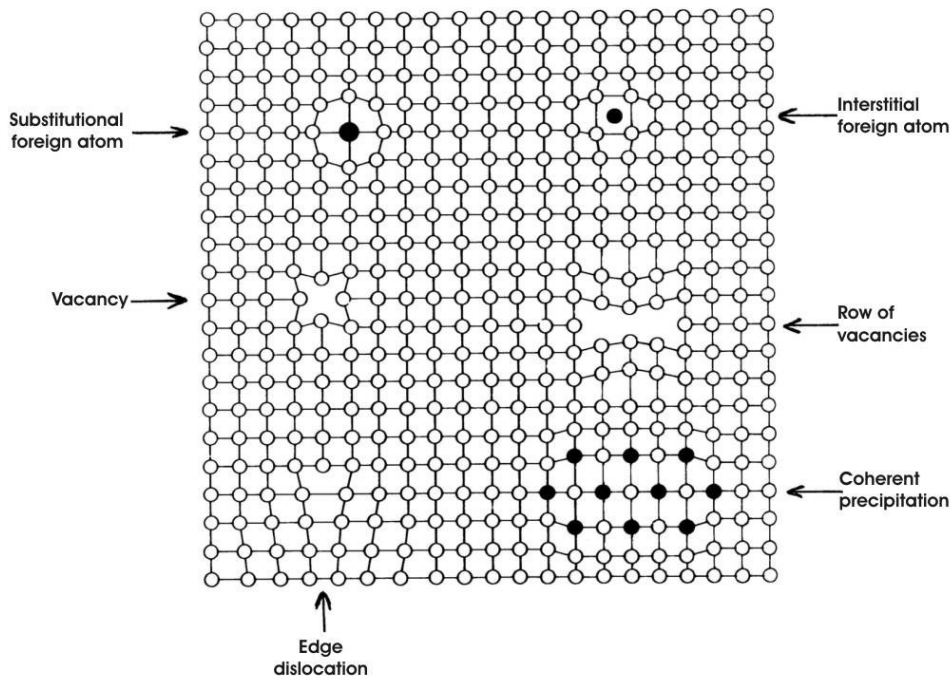


Figure 1-1. Schematic representation of some defects in an elemental solid. Adapted from Almar-Næss (1981).

Note how the defects tend to distort the structure around them, e.g. because the defect species is smaller or larger than the normal occupant. Thus, a point defect is associated with one structural site, but may comprise the distortions immediately around it.

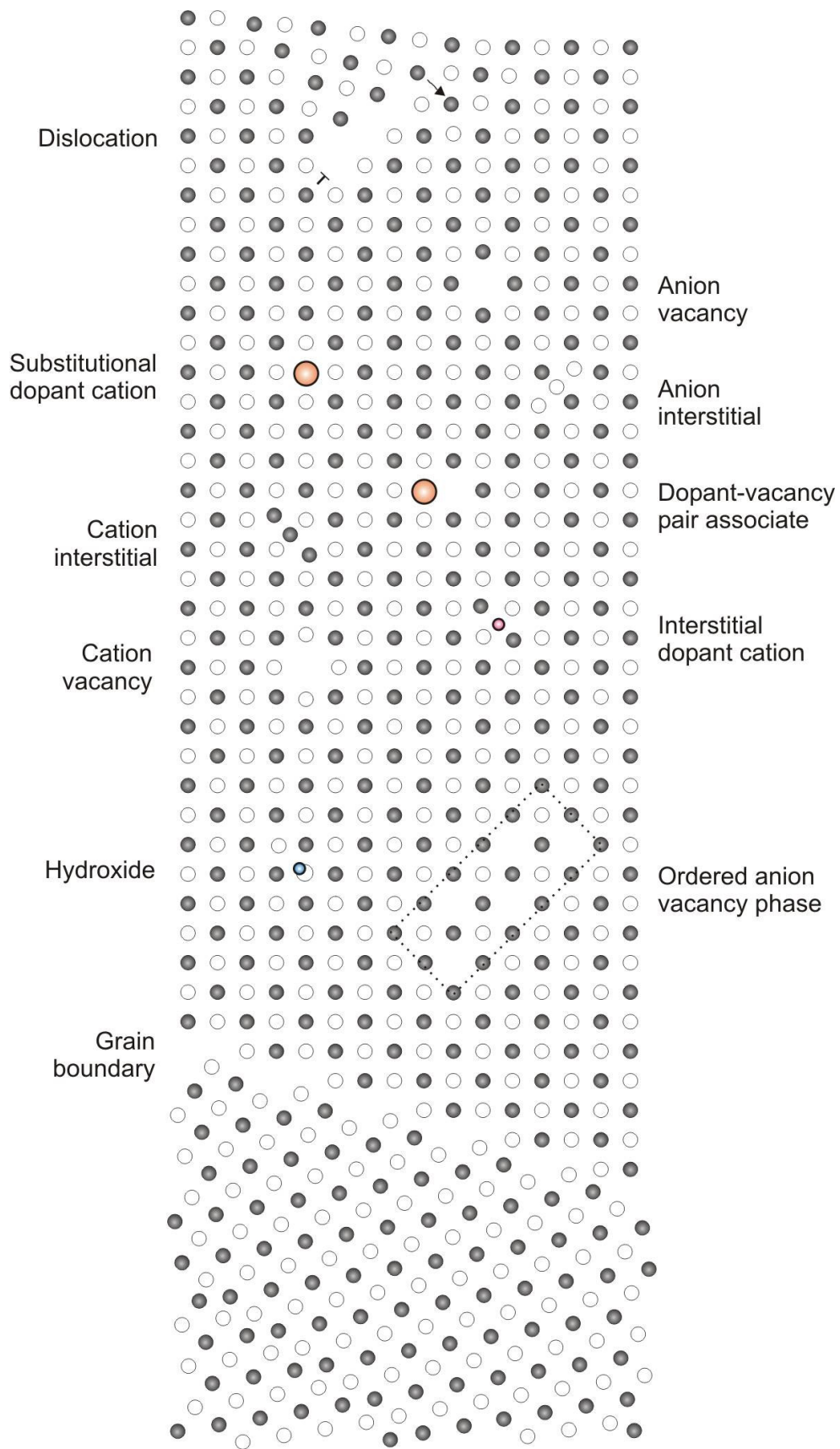


Figure 1-2. Schematic representation of some defects in an ionic compound MX . Cations M^{c+} are dark spheres, anions X^{z-} are open spheres.

Figure 1-2 shows a similar schematic structure with many defects, but now for an ionic compound MX, e.g. a halogenide like NaCl or a metal oxide like NiO. This brings in two types of interstitials and vacancies and more possibilities of foreign species. One of the foreign species is the proton, H^+ , which sits on a host oxide ion and forms a hydroxide defect. The figure depicts a dislocation and a grain boundary. In ionic compounds such higher-dimensional defects get very complex, as the figure indicates.

In addition to the structural defects, crystals may also contain *electronic defects*, i.e. *defect electrons* and *electron holes* that are relatively free to move in the crystal. The electronic defects may either be formed through internal excitation of valence electrons or they may be formed in association with point defects. If these electronic defects are localised (trapped) at regular sites in the structure, they are termed *polarons* or - from a chemical point of view - *valence defects*. Defect electrons or electron holes trapped at point defects often make otherwise transparent colourless materials coloured, and composite defects involving point defects and trapped electronic defects are in some branches of defect chemistry termed *colour centres*.

A complete description of the point and electronic defects in a compound and their concentrations as a function of the activities (partial pressures) of the constituents and the temperature is often termed the *defect structure* of the compound.

The reason for our interest in and concern with defects and imperfections is that they determine a number of properties of crystalline solids. Thus diffusion and ionic conductivity in crystalline solids take place because of the presence of defects. Point defects are responsible for lattice diffusion, dislocation diffusion takes place along line defects, and grain boundary and surface diffusion along planar defects. Solid state diffusion, in turn, determines or strongly influences a number of properties or processes such as mass transport in solids, solid state reactions, sintering, high temperature creep, gas-metal reactions resulting in the formation of compact layers of reaction products, etc. Electronic defects determine properties such as electronic conductivity, electro-optical properties, etc. Heterogeneous catalysis can be closely related to the defect chemistry of catalysts.

As a basis for further considerations of defect structures and defect-dependent properties to be discussed later, the remainder of this chapter briefly discusses some commonly occurring crystal structures in simple metal oxides, the notation of point defects, and qualitative descriptions of different types of defect structure situations. Later chapters will then derive and apply these situations more quantitatively.

Bonding in solids

Covalent, metallic, and ionic bonding

The bonding that makes up chemical compounds and condensed phases is a complex matter. Here we will include a brief overview of bonding in solids that may be helpful in understanding structure, valence, and charged defects.

When a bond is formed, it does so because the rearrangement of electrons between the partaking atoms when bonded causes a decrease in energy, compared to

the electron arrangement of the separate atoms. Only the noble gases find it most favourable to stay separate, as monoatomic atoms. All other elements find it better to bond the atoms to each other, thereby sharing electron pairs in overlapping (bonding) molecular orbitals with lower energy than the atomic orbitals. Examples are H_2 , F_2 , O_2 , N_2 , P_4 , and S_8 , in which the electron shell becomes complete by sharing electron pairs and completing the s- and p-orbitals with eight electrons (octet rule). The bonds are called *covalent* since the constituents have the same valency and share electrons equally. Covalent bonds can be categorised as strong bonds. These elements are rather gaseous, and condense only as the weak van der Waals forces between the molecules set in at decreasing temperature and increasing molecular weight. Some molecules become very big, as the C_{60} “football molecule”, C_n carbon tubes, and C_n layers of graphene. They can again be joined together into soft materials by weak forces between the layers, such as in graphite. Some covalent molecules stretch infinitely in all three dimensions, important examples being diamond (C) and silicon (Si). A crystal or grain of e.g. silicon is thus one macromolecule. Because of the strength of the covalent bonds some covalent macromolecule solids make up our hardest materials, such as diamond.

The electron pairs of the covalent bond are trapped in their very stable and directional orbitals, and find it difficult to find alternative states without gaining a lot of energy. Therefore the electrons have no mobility. To the first approximation covalently bonded solids thus have no conductivity and are insulators in their perfect state.

As we move to the left in the periodic table, the elements have fewer electrons in the outer (valence) shell to offer to bonding electron pairs, and they instead lower the energy more by sharing a sea of valence electrons with all atoms in the structure. The bonding of the condensed state that appears between all the atoms is called *metallic*. The deficiency of electrons makes available many unoccupied orbital states. These are delocalised over the structure and makes it easy to move around. The materials get high electronic conductivity, one of the typical metallic properties of the metals.

When elements explore energy minimisation by bonding to different elements, there are various possibilities to form compounds or alloys. If the elements are very similar to each other, especially regarding their ability to attract electrons in a bonding (electronegativity) they will probably make covalent bonds if they are both non-metals (in the upper right end of the periodic table) or metallic bonds if they are metals. Examples of covalently bonded solid compounds are silicon carbide, SiC, boron nitride, BN, and silicon dioxide SiO_2 . They are examples that elements of different valence may share electron pairs to satisfy the octet rule.

If the different elements are metals they may form alloys (a solid solution) if they are similar enough to be miscible in the solid state. Alternatively, and if present in stoichiometric, integer ratios, they may form so-called intermetallic compounds, e.g. $LaNi_5$ and $MgTi_2$.

Finally, if the different elements have very different electronegativities, the most electronegative will effectively take valence electrons from the less electronegative (also called more electropositive). For instance, Na will easily lose its one valence electron to Cl, which thereby fills its valence shell. Both are stabilised together as Na^+ and Cl^- ions. By this process, the Na shrinks considerably as its outer shell is emptied in becoming Na^+ , while the Cl grows considerably by the extra electron that repulses the other electrons and expands the outermost shell. However, the bond between the two ions would be weak as there is no overlap of electrons this way. But if many such pairs join and they are packed with alternating cation and anion side by side in a three-

dimensional structure, there is a total electrostatic energy gain. Packing cations and anions from gas phase into a structure is called the structure's lattice energy, and is a major part of the strength of the *ionic bond*. The packing of ions is rigid and the materials are in general hard (brittle). The electrons have in principle no possibilities to leave the anions, and the materials are generally insulators. The properties of typically ionic materials are termed salt-like.

One may note that metallic and ionic materials – as different as they are - have in common that they can be seen as non-directional packing of round spheres of atoms or ions. The ionic materials must accommodate small cations inbetween large anions, and the ration of the numbers of the cations and anions must obey charge neutrality, so they are typically less effectively packed and are generally less dense.

Another thing in common is that both the metallic and the ionic bonds are only well-defined in condensed phase, especially a solid structure. It is only the large number of the atoms or ions that enable these bonds to become well-defined and effective.

We have by this classified bonds and materials as being of three main classes: Covalent (share electron pairs between neighbours), metallic (share electrons between all atoms), and ionic (give or take electrons). In reality, no bond in a solid is fully metallic or ionic, it always has a degree of covalency (sharing between neighbours). Moreover, any covalent bond between different elements will have a degree of polarisation, i.e., a tendency of electrons being displaced towards one or the other element – normally a result of finite differences in electronegativity. The formation of polar covalent bonds can add electrostatic forces between the molecules to the actions of van der Waals forces, and make some compounds more easily condensed. The best known example is the polarisation of the water molecule that gives attractions between the positive proton ends and the negative oxygen ends, is called *hydrogen bonding*, and makes water and ice exist condensed at higher temperatures than one might otherwise expect from such a light molecule.

As a result of the variety, oxides for instance can take on many forms of bonding, and the classification is never simple. As said above, SiO_2 is a typically mostly covalent oxide. MgO and TiO_2 are more ionic oxides, but SrO and Na_2O are even more ionic. TiO has relatively unsatisfied bonds and orbitals and exhibits metallic properties. Despite this, the simple classifications into the three main groups of bonding is an extremely powerful tool for overview and first approaches.

Moreover, taking the concept of electronegativity to its full and extreme and treating all compounds as if they were fully ionic yields another tool; the formal oxidation number; the oxidation state (charge) an element would have in a bond if the most electronegative could take what it wants and the most electropositive can give what it can. The most electronegative elements are those with large nuclear charge combined with a small outer electron shell. These are to the right and to the top of the periodic table, with F as the most electronegative one. The least electronegative, most electropositive ones are at the diagonal opposite of the periodic table; the big atoms (far down) with relatively small nuclear charge (to the left). From this, formal oxidation numbers are assigned based on a few simple rules:

- F has formal oxidation number -1 (fluoride) in all compounds.
- O has formal oxidation number -2 (oxide) , -1 (peroxide) or -1/2 (superoxide), except in a bond with F.

1. Bonding, structure, and defects

- H has oxidation number +1 or -1.
- All other oxidation numbers follow based on magnitude of electronegativity and preference for filling or emptying outer shell.

All in all, the electronegativity and valence (the number of electrons desired or offered) are the chemist's first approach to predicting the stability and properties of simple compounds. The periodic table and the elements' placement there is the primary tool for this.

The formal oxidation number gives a simplified picture of the charges of ions...the real distribution between the more electronegative and the more electropositive – the ionicity – is usually far from the purely ionic model. Nevertheless, the ionic model approximation predicts the stoichiometric ratios between elements remarkably well.

Moreover, as we have stated before and will come back to later, defect chemistry works remarkably well under an ionic model approximation that enables all species including defects to take on integer charges. The reason for this is that even if all bonds has a non-integer distribution of electrons on the two atoms, an electron cannot be split; it must be in the neighbourhood of a defect or not. If the species or defect moves, an electron associated with it has to move or stay; everything that goes on goes on by integer charges (whole electrons).

As we shall see later on, the size of the atoms and ions is the factor that additionally enables prediction of the stability of structures with metallic and ionic bonding, and an understanding of how sizes vary through the periodic table and with charge of ions completes the tools for the solid-state chemist and materials scientist.

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids	* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb				
**Actinoids	** 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No				

Figure 1-3. Periodic table of the elements. The group number counts electrons in the two outermost shells. For groups 1-2 and 13-18 the last digit gives account of the sum of the number of outermost shell *s* and *p* electrons, where simple preferences for valence can be evaluated. For groups 3-12 the number gives account of the sum of outermost *p* and underlying *d* electrons, and where resulting valence preferences are more complex.

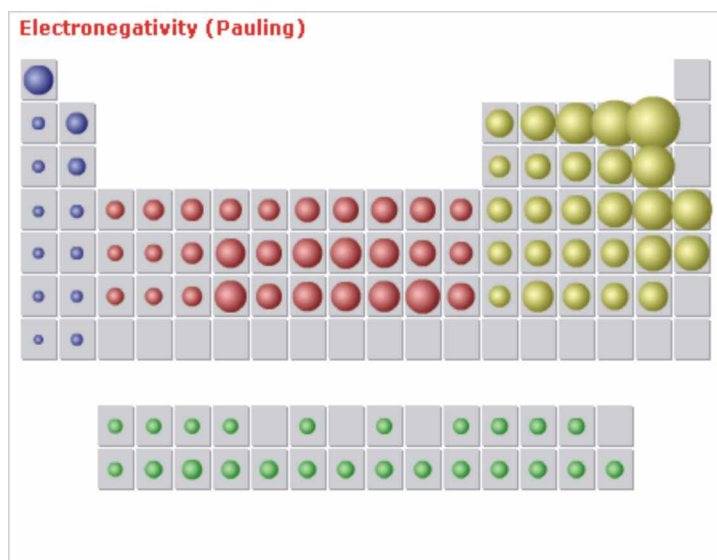


Figure 1-4. Electronegativities of the elements of the periodic table represented graphically by the size of the spheres. From <http://www.webelements.com>.

Electron energy bands

While we are dealing with bonds, it is useful to look at the energy levels of electrons as atomic orbitals develop into molecular orbitals and further into bands of molecular orbitals as bonds and solids form. From quantum mechanics, free electrons can have any energy, but as they become restricted to orbitals around a nucleus, only discrete energies are possible. Energies in separated atoms can be the same, but as they become bonded, new orbitals are formed. They are as many as there were contributing atomic orbitals, and the electrons must all occupy different energies. As we form a solid – either by imagining that we bring in more and more atoms in the structure, or by bringing a large number of atoms closer and closer – the different energies become closer and closer to accommodate all the electrons. They form bands of allowed electron energies. There may be regions in energy which have no allowed states. These gaps typically separate different main shells and geometrically different types of orbitals. The lowest-laying bands are narrow and with energies that reflect close to atomic orbitals. The outermost band that contains electrons – the electrons with the highest energy – is called the *valence band*. It mainly consists of the valence electrons of the participating atoms.

In phases with metallic bonding, there are not enough electrons to fill up all the available energy levels in the band that has been constructed from all the valence orbitals. The valence band comes out as partially occupied. In this situation there is – as said earlier – plenty of opportunity to take available levels without much extra energy – and we have metallic mobility of electrons.

In phases with ionic or covalent bonding, the valence electrons are well-localised in ions or in bonding electron-pairs and fill up all energy levels available. There is usually a big jump in energy to the next level...that would typically reflect anti-bonding orbitals or another oxidation state of an ion. This next level – the lowest band that is

empty in the ground state – is called the *conduction band*. Its name indicates that electrons that would end up here would be free to take on other empty state close in energy and be mobile...they would give rise to electronic conductivity.

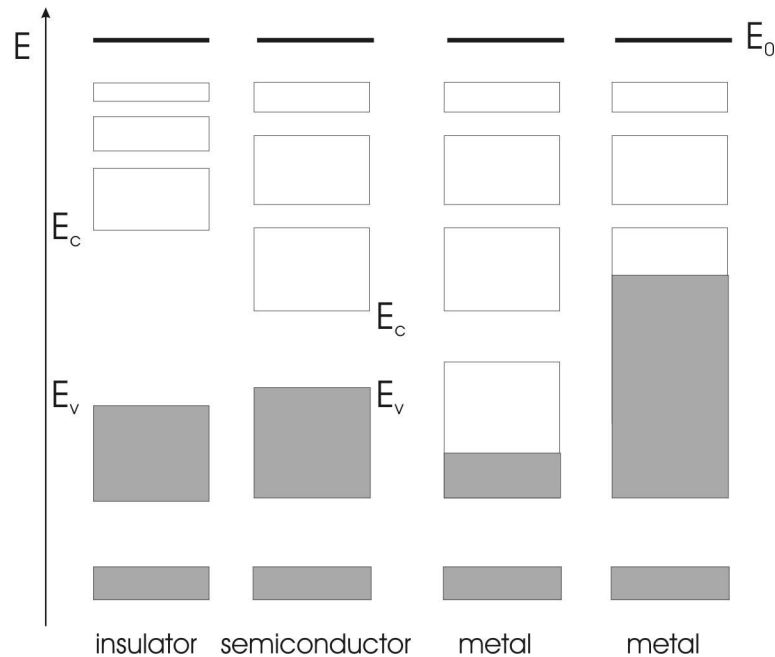


Figure 1-5. Schematic band structures. E_c and E_v are the conduction and valence band edge energies. E_0 is the vacuum energy level of electrons.

Common crystal structures

Close-packing and voids

The crystal structures of many metals and semiconductors can be described by close-packing of spheres (atoms). Similarly, many simple oxides to be discussed later can conveniently be considered to consist of close-packing of oxide ions while the metal ions occupy voids in the close-packed structures. Let us therefore briefly discuss close-packing of spheres (atoms or ions).

Consider an atom as a small hard sphere and make a layer of identical atoms so that the empty space between the atoms is minimum (layer A). Let us now add a second layer (B) such that the atoms in this second layer sit in one set of the hollows of the first layer, see Figure 1-6. When we add a third layer of spheres, the spheres can be placed in two different positions: the spheres in the third layer can be placed directly over the spheres in layer A, and if we continue this stacking, the stacking sequence becomes ABAB.... The third layer (layer C) could alternatively be placed such that the spheres in this layer will not be directly over either the atoms in the A or B layers, see Figure 1-6. The stacking sequence is now ABCABC....

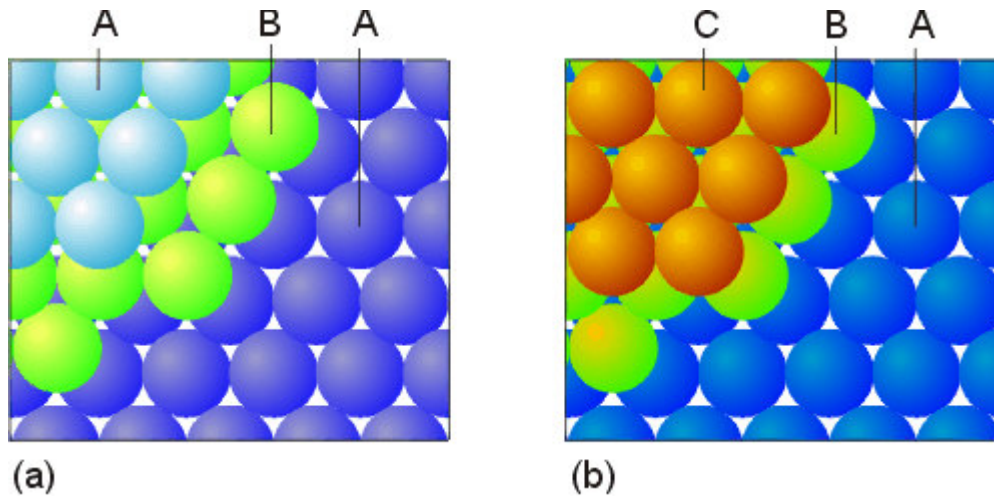


Figure 1-6. ABABAB...(hcp) close-packing (a) and ABCABC...(fcc) close-packing (b) of spheres. From Shriver and Atkins (1999).

The ABAB close-packed stacking is called hexagonal close packing (hcp) of the spheres because it gives crystal structures with hexagonal symmetry, see Figure 1-7. The ABCABC close packing is known as cubic close packing (ccp) as this gives rise to a cubic (face-centred) crystal structure when the hexagonal planes are viewed with a 45° tilt, See Figure 1-7.

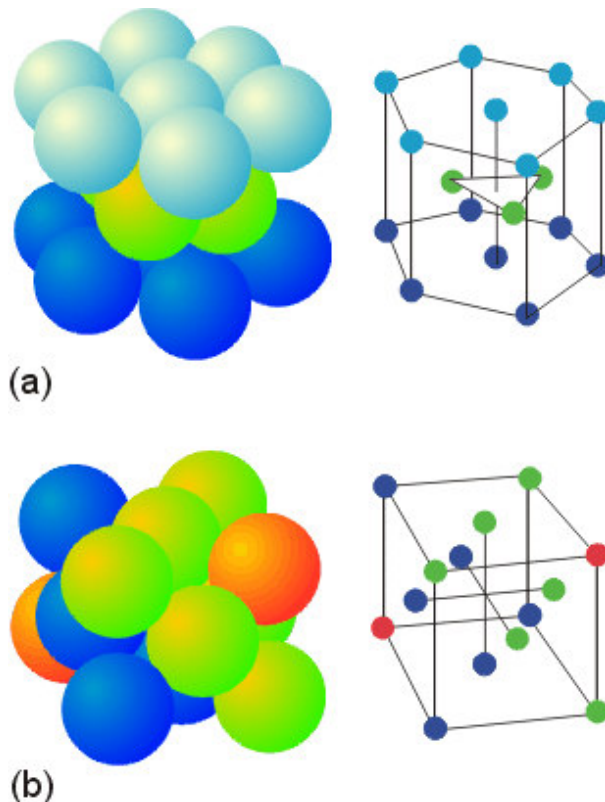


Figure 1-7. Schematic views of the hcp (a) and fcc (b) structure types. From Shriver and Atkins (1999).

The close-packed structures contain two different types of empty space or voids (also sometimes called interstices) between the spheres, cf. Figure 1-8. One type of void is called an octahedral void. In this case each void is surrounded by six spheres, three in one layer and three in the neighbouring layer, and the centres of these six spheres lie at the corners of an octahedron. Another type of void is termed tetrahedral void because each of these are surrounded by four spheres which centres are at the corners of a tetrahedron. In the close-packed structures there are two tetrahedral voids and one octahedral void per atom (sphere). It may be noted that an octahedral void will fit a sphere with radius $0.414r$ where r is the radius of the bigger close-packed spheres. A tetrahedral void is smaller and may fit a sphere with radius $0.225r$.



Figure 1-8. Octahedral (left) and tetrahedral (right) void in close-packed layers of spheres.

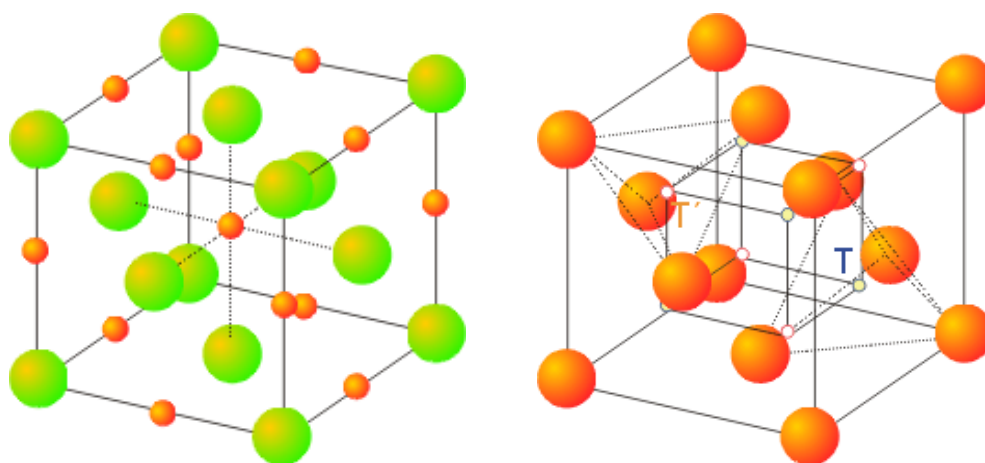


Figure 1-9. Small spheres show locations of octahedral (left) and tetrahedral (right) voids in the fcc structure. From Shriver and Atkins (1999).

In crystal structures of simple metal oxides which can be considered to consist of a close-packing of oxygen atoms, the metal ions often occupy all or part of the tetrahedral and/or octahedral voids in regular patterns. It is important to realize that structural ions occupying such voids are not to be considered as interstitial defects – they are part of the ideal crystal structure.

Less close-packed arrangements

Some metals and ionic compounds choose to arrange themselves in less close-packed structures, as exemplified in the following two figures.

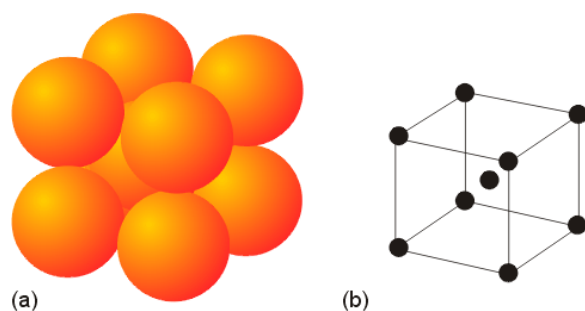


Figure 1-10. Body-centered cubic (bcc) packing of spheres. From Shriver and Atkins (1999).

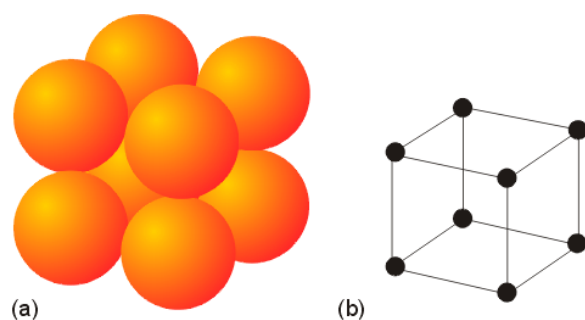


Figure 1-11. Simple cubic (sc) packing of spheres. From Shriver and Atkins (1999).

The reasons for such less close-packed structures can be increased temperature, some directionality in bonding, or occupancy of relatively big species in the voids.

Also less close-packed structures have voids; they may be bigger and with different coordination than in the closest packings. For instance, the simple cubic structure (Figure 1-11) has 8-coordinated hexahedral voids in the centre of each cube.

Some simple structures for oxides and other ionic compounds

As mentioned earlier, the structures of ionic compounds can often be seen as close-packing of the large anions, while the normally smaller cations occupy the interstitial voids. (We repeat that once the structure is established, the voids occupied by these cations are not any longer considered interstitial; they are part of the ideal reference structure.)

In judging the packing of ions it is useful to recall some important principles of ionic radii; the size of the elements increase down a group of the periodic table (resulting from the larger orbital of the outermost shell). Further, the size of the elements as a rule of thumb decreases from left to right through a period of the periodic table (resulting from increased nuclear charge). Finally, and most importantly in this context: Negatively charged ions (anions) are much larger and positively charged ions (cations) are much smaller than the corresponding neutral atoms. One may also recall that the effective size increases with the coordination number (Shriver and Atkins (1999)). In the following we look at some example structures possessed by metal oxides and other ionic compounds.

The NaCl (rock salt, halite) structure

In the NaCl structure the anions are cubic close-packed (fcc), and the smaller metal ions occupy all the octahedral interstices. Each metal ion is thus surrounded by six anions and vice versa. The NaCl structure is illustrated below. Note the similarity with the illustration of the octahedral voids in the fcc structure shown previously.

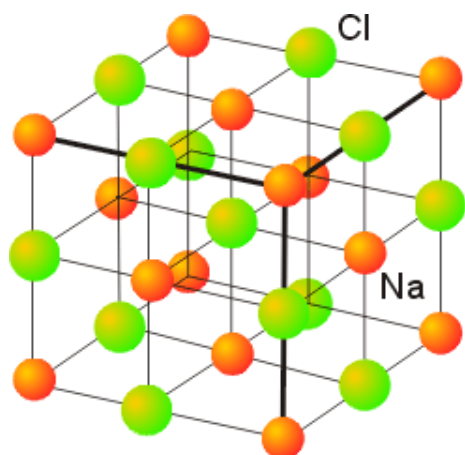


Figure 1-12. The NaCl structure. Note that the centre anion is six-coordinated, as are also all other ions. From Shriver and Atkins (1999).

In addition to many AX halides, the oxides MgO, CaO, SrO, BaO, CdO, CoO, NiO, FeO, TiO, NbO, and VO possess this crystal structure. The last six of these oxides may be highly nonstoichiometric and as such their NaCl-type structures highly defective.

In the sulfides FeS and NiS, the structure is similar, but the close-packing of anions is hexagonal (hcp) rather than cubic.

The ZnS (zinc blende and wurtzite) structures

These structures are named after two different mineral forms of zinc sulphide (ZnS). The zinc blende structure can be considered as a cubic close-packing of sulphide ions with the zinc ions occupying every other tetrahedral void. Each zinc ion is thus tetrahedrally coordinated by four sulphide ions and vice versa.

The wurtzite structure is composed of hexagonal close-packed sulphide ions and where zinc ions occupy every other tetrahedral void. The metal oxides BeO and ZnO adopt the wurtzite structure.

The CaF₂ (fluorite) structure

The fluorite structure is named after the mineral calcium fluoride (CaF₂) and is illustrated below. Crystallographers often consider it to constitute a face-centered close-packing (fcc) of the metal ions while the anions occupy all the tetrahedral sites. However, the calcium ions are smaller than the fluoride ions and the fluoride ions do not really fit into the voids of the calcium ion array, but the model describes the relative positions of the ions, see Figure 1-13. For us it is more useful to view the structure as a

simple cubic (sc) packing of anions (not close-packed), with cations filling every other cubic void. This can also be seen in Figure 1-13 if one considers the cube of the fluorines being an empty one, while the next ones will have calcium ions in their centres.

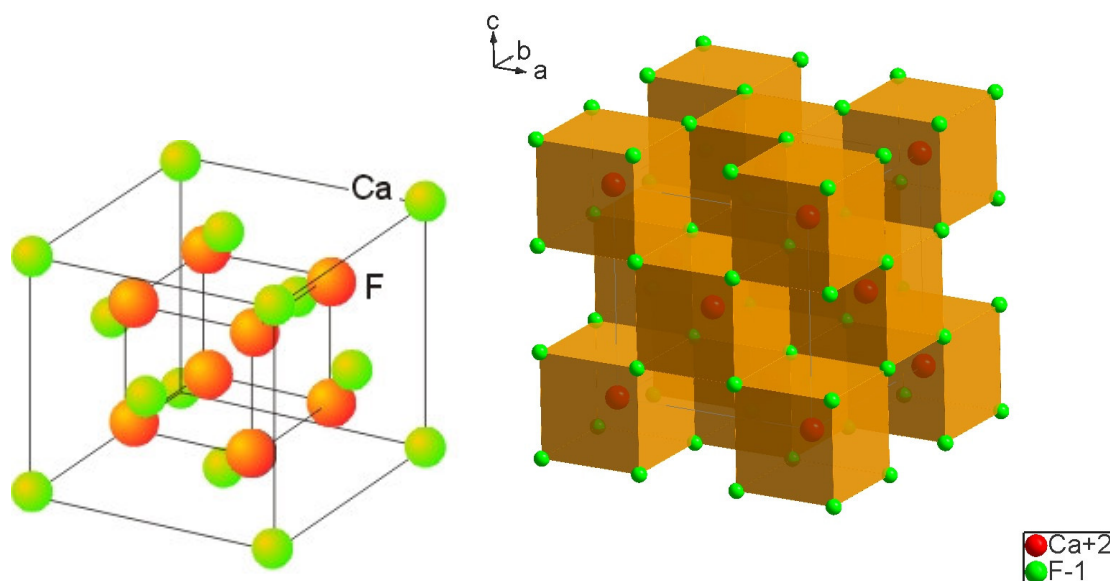


Figure 1-13. The CaF_2 structure. Left: In this view, the Ca cations form an fcc sublattice, while the F anions form a simple cubic arrangement in the tetrahedral voids. Right: If we instead take anions to form a simple cubic packing, every second anion cube has a cation in its centre.

The fluorite structure is typical for AX_2 compounds where A is a sufficiently large cation that it forces the anions apart and into a less than close-packed arrangement. ZrO_2 , HfO_2 , CeO_2 , ThO_2 , and PuO_2 are important examples of oxides which possess the fluorite structure (some of them only at elevated temperatures or with proper concentrations of certain defects). All the octahedral voids are unoccupied for the stoichiometric compositions, but interstitial ions may be accommodated in these interstices and form oxides with excess oxygen (hyper-stoichiometric oxides), e.g. UO_{2+x} .

Pyrochlore ($\text{ABO}_{3.5}$) and C-type rare earth sesquioxide (A_2O_3) structures can be viewed as fluorite-derived structures with, respectively, 1/8 or 1/4 of the oxide ions missing (in an ordered fashion).

The alkali metal oxides Li_2O , Na_2O , K_2O , and Rb_2O possess the so-called anti-fluorite structure. In this structure the oxide ions can be considered to be cubic close-packed (fcc) while the metal ions occupy all the tetrahedral voids.

The rutile (TiO_2) structure

The rutile crystal structure has its name after the rutile modification of titanium dioxide, TiO_2 . It is based on a hexagonal close-packing (hcp) of the oxide ions, with Ti ions occupying every second octahedral void, so that the structure can be viewed as consisting of TiO_6 octahedra (slightly distorted) which share edges and corners in such a way that each oxygen atom belongs to three neighbouring octahedra. The structure

has a tetrahedral unit cell, and when the structure is viewed along the c-axis it may be seen that the structure contains channels in the c-direction, i.e. rows of oxide ion octahedra not filled with cations.

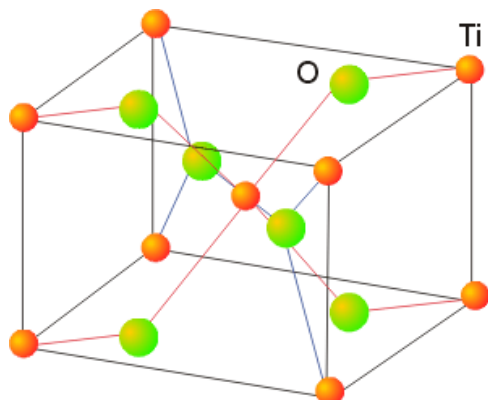


Figure 1-14. The rutile TiO_2 structure. From Shriver and Atkins (1999).

In addition to rutile (TiO_2) itself, SnO_2 , MnO_2 , VO_2 , MoO_2 , RuO_2 , GeO_2 are examples of oxides which possess regular or distorted rutile structures.

The corundum ($\alpha\text{-Al}_2\text{O}_3$) and ilmenite (FeTiO_3) structures

The corundum structure is named after the high-temperature modification of alumina, $\alpha\text{-Al}_2\text{O}_3$. This structure may be described as a hexagonal close-packing (hcp) of oxide ions with the trivalent aluminium ions occupying $2/3$ of the octahedral sites. As the cations occupy octahedral sites, each cation is octahedrally coordinated and surrounded by six oxide ions, while each oxide ion is surrounded by four cations. Two and two cations occupy neighbouring octahedral voids, and the two corresponding AlO_6 octahedra are linked by common faces. Other oxides possessing the corundum structure are $\alpha\text{-Fe}_2\text{O}_3$, Cr_2O_3 , Ti_2O_3 , and V_2O_3 .

A number of oxides with the nominal formula ABO_3 have the corundum structure when A and B have an average valence of 3 and are of approximately the same size. The ilmenite structure with the nominal formula ABO_3 and named after the mineral $\text{Fe}^{\text{II}}\text{Ti}^{\text{IV}}\text{O}_3$ is similar to the corundum structure in that the oxide ions can be described as hexagonal close-packed, the valences of the two cations have an average valence of 3 and occupy $2/3$ of the octahedral sites. However, in this case the two metal ions (Fe^{2+} and Ti^{4+}) are arranged in alternate layers.

The spinel structures

The spinel structure is named after the mineral spinel, MgAl_2O_4 . The spinels have the general formula AB_2O_4 , where A is most often a divalent ion, A^{2+} , and B trivalent, B^{3+} . The oxide ions can be considered to be cubic close-packed (fcc), and the metal ions occupy both tetrahedral and octahedral sites. The unit cell contains 32 oxygen atoms, 8 AB_2O_4 units. It contains 32 octahedral and 64 tetrahedral voids. In the

normal spinel structure one half of the octahedral voids are occupied by the B^{3+} -ion while the A^{2+} ions occupy 1/8 of the tetrahedral voids.

Other distributions of the cations occur. When the eight tetrahedral sites per unit cell are occupied by trivalent cations and the octahedral sites are shared by the divalent and trivalent ions, the structure is termed an inverse spinel. Magnetite, Fe_3O_4 , is an example of an inverse spinel. An inverse spinel may be better written as $B(AB)O_4$ as this indicates that half of the B^{3+} ions occupy tetrahedral sites and the other half together with the A^{2+} ions occupy the octahedral sites. Another example of an oxide with inverse spinel structure is $MgFe_2O_4$ (or $Fe(MgFe)O_4$).

If the general formula of the spinel is written AB_2O_4 , the cations may have the valence A^{2+} and B^{3+} as discussed above. This is termed a 2-3 spinel. In addition one may have spinels with other cation valences, e.g. A^{4+} and B^{2+} (4-2 spinel) and with A^{6+} and B^{1+} . In all cases the sum of the cation valences equals 8.

The perovskite ($CaTiO_3$) structure

The perovskite structure has its name after the mineral perovskite, $CaTiO_3$. The general formula may be written ABO_3 in which A is a large cation (e.g. alkali, alkaline earth, rare earth ions) and B a small or medium sized metal ion often a transition metal ion. In this structure the large A cations and oxide ions together form a cubic close-packed (fcc) lattice, such that each A cation is coordinated to twelve oxide ions. The B cations occupy octahedral sites surrounded by six oxide ions.

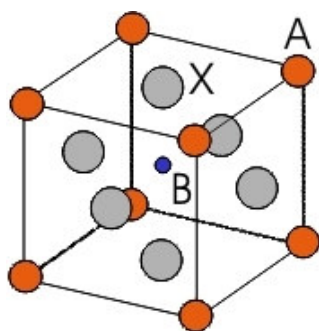


Figure 1-15. Perovskite ABX_3 structure. Shown as an fcc packing of A (corners) and X (faces) atoms, with the B in the center.

The sum of valences on the A+B cations is +6, so that the average valence of the A and B ions is +3. The perovskite structure is remarkable in being very tolerant to variations (as long as A is large and B is small). Thus, A+B valences can be 3+3 (e.g., $LaAlO_3$), 2+4 (e.g. $CaTiO_3$), 1+5 (e.g. $KTaO_3$) and even 0+6 (where the A site is in fact empty, as in WO_3).

The perovskite structure tolerates relatively large nonstoichiometries and substitutions, while a number of perovskite-related structures (with perovskite building blocks) are formed when excesses, deficiencies or substitutions beyond the solubility limits lead to ordered defects and new phases. These comprise, for instance, oxygen deficiency (brownmillerite, $ABO_{2.5}$) and A excess (K_2NiF_4 -type structure, A_2BO_4)

and series of ordered phases intermediate in composition between these and the normal perovskite.

Summary of relations between structures, radii and packing arrangements.

In oxides with small cations only, the structure is dominated by close-packing of the oxide ions and various occupancies of voids by the small cations. The table below summarises relations between structures and close-packed arrangements of anions or cations in oxides and some sulphides.

Table 1-1. Some structures of oxides based on close-packed oxide ion sublattices.

Formula	Cation:anion coordination	Type and number of occupied voids	fcc of anions	hcp of anions
MO	6:6	1/1 of octahedral voids	NaCl, MgO, CaO, CoO, NiO, FeO a.o.	FeS, NiS
MO	4:4	1/2 of tetrahedral voids	Zinc blende: ZnS	Wurtzite: ZnS, BeO, ZnO
M ₂ O	8:4	1/1 of tetrahedral voids	Anti-fluorite: Li ₂ O, Na ₂ O a.o.	
M ₂ O ₃ , ABO ₃	6:4	2/3 of octahedral voids		Corundum: Al ₂ O ₃ , Fe ₂ O ₃ , Cr ₂ O ₃ a.o. Ilmenite: FeTiO ₃
MO ₂	6:3	1/2 of octahedral voids		Rutile: TiO ₂ , SnO ₂
AB ₂ O ₄		1/8 of tetrahedral and 1/2 of octahedral voids	Spinel: MgAl ₂ O ₄ Inverse spinel: Fe ₃ O ₄	

When the cations get somewhat larger they force the anions apart, and we get non-close-packed structure types like the fluorite and its derivatives (pyrochlore, rare-earth oxide structures, etc.)

When we involve even larger cations, being of the same size as the anions, the large cations take part in the close-packing together with the anions. In this way we get the perovskite structure and its derivatives (brownmillerite, K₂NiF₄-type, etc.)

More detailed treatments on crystal structures of oxides are found in general texts on solid state chemistry (e.g. Smart and Moore (1992) or West (1984)) and in more specialised literature, such as N aray-Szab  (1969) and Rao and Raveau (1995).

Point defects and Kröger-Vink notation

In order to understand and describe properties of crystalline solids that are dependent on the presence of point defects, it is necessary to be able to express the concentrations of the defects under various conditions. This requires a system of notation to describe the point defects and the constituent atoms of the structure and their charges.

Kröger-Vink notation; content and site

In the development of the field of defect chemistry of inorganic compounds various systems of notation have been proposed and used to describe point defects. However, the most widely adopted system is that due to Kröger and Vink (1956) (see also Kröger (1964)), and this will be used in this book. This system describes crystals in terms of structural elements, and all such elements (atoms or ions) are identified in terms of *what* they are (their chemical content) and *where* they are (what kind of structural position they occupy). This is indicated by a major symbol describing the chemical content and a subscript that indicates the site that it occupies.

In an oxide the metal ions on the regular lattice positions are thus written M_M , where the subscript thus describes the type of structure site which is occupied. Correspondingly, the oxide ions on normal lattice sites are written O_O . These are not defects, they are the ideal structural elements.

The native point defects in an oxide include M and O vacancies and M and O interstitial atoms or ions. Vacancies in binary oxides are denoted by “v” with a subscript M or O referring to vacant metal or oxygen sites, respectively:

v_O oxygen vacancy,

v_M metal vacancy,

Interstitial sites are described with a subscript “i”. Interstitials in a binary oxide are thus written

O_i oxygen interstitial,

M_i metal interstitial.

Correspondingly, an unoccupied (vacant) interstitial site can be written v_i . This is again not a defect; interstitial sites are empty in the ideal structure.

One may find that literature upto this text has used uppercase V for vacancy and I for interstitial site. However, this creates confusion with the elements vanadium (V) and iodine (I). While defect chemistry of vanadium compounds and iodides was too exotic when Kröger and Vink created the symbol sets, they are less exotic today, and their defect chemistry would be difficult to read with the uppercase symbols (and for vanadium iodides it would be hilarious!) One can circumvent the problem by using italics or odd V- or I-like symbols, but using lowercase symbols is simple, has no complications, and is formally correct since neither the v for vacancy or i for interstitial

site represent a chemical symbol. Hence, we will use the lower case v and i here, and I suggest it becomes a standard development of the Kröger-Vink notation.

Component atoms of a crystal may find themselves on the wrong site; the A and B cations in perovskite, pyrochlore, spinel, etc. may thus swap sites so as to obtain A_B and B_A . An oxygen atom in a metal site is similarly written O_M , but is an example of a very unstable defect.

Real crystals always contain impurities. When a foreign metal atom M_f occupies a regular M site, the foreign atom is denoted by M_f_M . If it occupies an interstitial site, it is described by M_f_i .

Kröger-Vink notation; real and effective charge

In an ionic compound the atoms are charged, and the cations and anions may be assigned a definite integer valence (formal oxidation number). This is in fact a fully valid model in defect chemistry, as will be argued in a discussion on the influence of the varying degree of ionicity, or distribution of valence electrons, in a later paragraph.

Oxide ions on regular sites in an oxide have a formal valence of -2. The cations have formal positive charges so as to make the sum of all positive and negative charges in the compound equal to zero.

The normal structural elements as well as point defects may be neutral or charged. Their charges may be described in terms of their real actual charge or valence. However, it is generally more convenient in writing defect reactions to use the ideal, perfect crystal as the reference state and consider the charge on the defects relative to this perfect crystal. This relative charge is termed the effective charge of the defect. With the perfect crystal as reference, the normal atoms on regular lattice sites have zero effective charge. To emphasise this zero effective charge, an "x" is often added as a superscript to the symbol. The normal cations and anions in an oxide are then written M_M^x and O_O^x .

When vacancies are present, part or all of the actual charge of the missing atom may be excited away from the vacant site. Let us, for instance, consider the formation of an oxygen vacancy by removing an oxygen atom from the crystal. If the two electrons of the oxide ion are localised at or near the empty site, the vacancy and its immediate neighbourhood have two negative actual charges. The charge at this location is thus the same as in the perfect crystal and the oxygen vacancy then has zero effective charge. As such it is termed a neutral oxygen vacancy, which is written v_O^x .

Now that the electronegative oxygen atom is no longer present to hold the extra electrons, one or both of the two electrons can easily be excited and transferred away from the oxygen vacancy, and the oxygen vacancy then becomes singly or doubly charged. Since electrons are removed, the ionised vacancy has an effective positive charge relative to the perfect crystal, compensated by the two electrons which are now negatively charged defects somewhere out in the crystal.

The effective charge of a species is the actual charge of the species minus the actual charge that the ideal perfect reference structure would have had in the same structural element.

To distinguish effective from actual charges, different symbols are used. While the actual charges are written + or -, the effective positive charge is indicated by a subscript dot (\bullet) and the effective negative charge by a superscript slash or prime ($'$).

Singly and doubly charged oxygen vacancies are, thus written v_o^\bullet and $v_o^{\bullet\bullet}$, respectively.

Similarly, cation vacancies may be neutral or have negative effective charges. To illustrate this let us remove a metal atom from the oxide MO and create a vacant metal ion site. The M^{2+} ion picks up two electrons to leave as an atom, leaving behind two positive charges in the form of holes or valence defects. If these are localised at neighbouring oxide ions (as O^-) or metal ions (as M^{3+}) the actual charge at the vacancy and its immediate neighbourhood is then the same as in the perfect crystal, and the effective charge on the metal vacancy is considered to be zero, i.e. the metal vacancy is neutral, v_M^x . One or both of the positive charges may be excited and transferred away from the vacancy and distributed in the oxide, and the vacancy then has one or two negative effective charges and is written as v_M' or v_M'' , respectively.

Similarly, interstitially dissolved atoms will have zero real and effective charge, but depending on their nature they can be ionised to cations with a real and effective positive charge or to anions with real and effective negative charge.

Substitutionally dissolved foreign ions which tend to have a valence different from that of the normal ions (aliovalent foreign ions) are easily ionised to get an effective charge. For instance, if the valence of a substitutionally dissolved foreign cation is higher than that of the normal host cation, the foreign cation gets a positive effective charge. Conversely, if the valence of the substitutionally dissolved foreign ion is smaller than the host cation, the foreign cation gets a negative effective charge.

As an example, consider ZrO_2 . If we substitute some of the zirconium with yttrium, the yttrium will obey its valence and become an Y^{3+} ion on the site of the Zr^{4+} ion. It thus becomes effectively negative; Y_{Zr}' . If we alternatively substitute Zr^{4+} ions with Nb^{5+} , the defect becomes Nb_{Zr}^\bullet .

Kröger-Vink notation; semiconductors - electrons and holes

Important examples are also found in the semiconductor field, e.g. in the semiconductor silicon (Si). The principles are the same, one just have to remember that the ideal structure contains Si in the elemental, neutral state, Si^0 , or, in Kröger-Vink notation, Si_{Si}^x . Boron (B) atoms dissolved in silicon as B^0 is denoted B_{Si}^x in the unexcited state. But since boron has one valence electron less than the surrounding Si^0 atoms it easily accepts one from the valence band of the Si lattice in order to fulfill the octet rule and becomes B^- or, in Kröger-Vink notation, B_{Si}' . Boron is therefore called an electron acceptor (acceptor dopant) and the lacking electron in the valence band is called a hole. In a similar way, phosphorous forms a donor in silicon; P_{Si}^x and the excited state is P_{Si}^\bullet when it has donated an electron to the conduction band. Figure 1-16 attempts to illustrate the bonding valence electrons for Si with B and P dopants, with

the lacking electron (hole) and extra electron drawn located at the acceptor and donor dopant atoms before the ionisation to delocalise the hole and electron.

Defect electrons (extra electrons in the normally empty conduction band) and electron holes (lacking electrons in the otherwise full valence band) that are free to move in the oxide have effective negative and positive charges, respectively. They are written e' and h^\bullet . If the electron, for instance, is associated with a cation on a regular site - and may as such be considered a valence defect - the defect may be written M_M' .

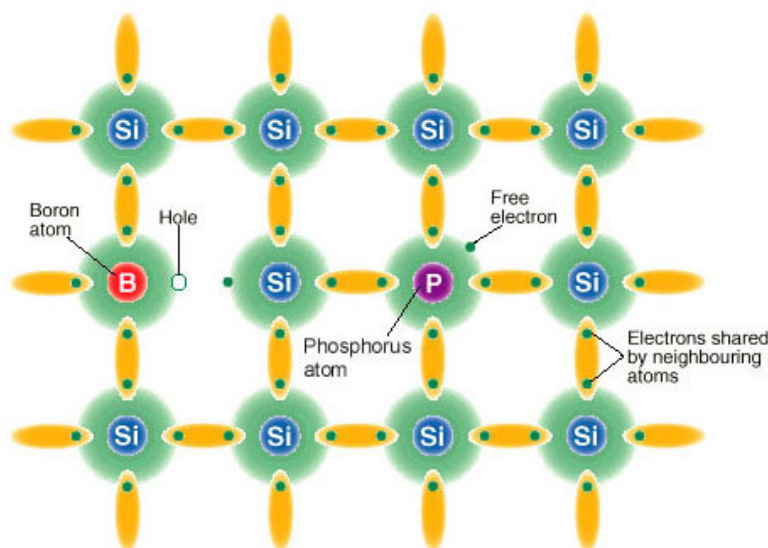


Figure 1-16. Schematic view of electronic structure of boron- and phosphorous-doped silicon. From <http://acrc.murdoch.edu.au/refiles/pv/text.html>

Kröger-Vink notation; protonic defects

In this text we will deal with protons, H^+ , and they require somewhat special treatment, since they consist of a naked nucleus, only 1/100000 of the size of any other chemical species (atom or ion). Any proton will in a chemical environment always be attracted into the electron cloud of a nearby atom or ion. In oxidic materials this will normally be by an oxide ion, and protons are thus always present as OH^- ions or – mostly in aqueous and liquid phases - as H_2O molecules or H_3O^+ ions. In a hydroxide, such as $Ca(OH)_2$, we may assign a structural site to the proton, or consider the hydroxide ion as a unit, with a structural site.

In an oxide, on the other hand, the proton is a foreign species, a defect. They are so small that they may not occupy a structural site and they may thus not substitute any cation. They may only go in interstitially and will then be effectively positive. We may thus denote the defect H_i^\bullet . But they are too small to remain at a normal interstitial site in the center of voids, they will be drawn into the electron cloud of an anion such as an oxide ion and form a hydroxide ion, as attempted illustrated in Figure 1-2. The defect is in this case a hydroxide ion OH^- substituting an oxide ion O^{2-} , and the defect notation is thus $(OH)_O^\bullet$ or, for simplicity, OH_O^\bullet .

The terms substitutional hydroxide OH_o^\bullet and interstitial proton H_i^\bullet are used side by side, which does not pose any problem as long as one is aware of the real situation. As we shall see later on, the hydroxide notation is suitable to describe defect statistical thermodynamics, while the interstitial proton is more suitable to describe its transport, because the proton jumps from oxide ion to oxide ion, leaving the host oxide ion behind.

Kröger-Vink notation; summary table

The table below attempts to summarise the symbols we use in Kröger-Vink notation.

Table 1-2. Overview of Kröger-Vink notation A_s^c

Content A	Structural site s	Charge c	
		Real	Effective
Element symbol H, He, Li...Pa, U... or vacant: v electron: e electron hole: h	Element symbol: H, He, Li...Pa, U... or interstitial: i	Positive +	Positive •
		Negative -	Negative /
		Neutral	Neutral x

Electroneutrality

Crystals that we will deal with are considered to be electrically neutral. Then the sum of all positive charges must equal the sum of all negative charges:

$$\sum \text{positive charges} = \sum \text{negative charges}$$

We may thus sum up the real charges of all cations and anions and defects. However, it is equivalent and more convenient to consider only the effective charges:

$$\sum \text{positive effective charges} = \sum \text{negative effective charges}$$

It is important to note that the number of positive and negative charges must be compared on equal basis, namely as concentrations (numbers of species or number of moles per volume). One may in general *not* use site fractions since the concentrations of different types of sites are not necessarily equal. Thus, the electroneutrality condition can be expressed as

$$\sum_s z[s^z] = 0 \quad (1.1)$$

where the brackets denote concentration and z is the charge on the species s^z . For instance, in an oxide MO where the major defects are oxygen vacancies, metal interstitials, and defect electrons, the electroneutrality condition can be written

$$2[v_o^{\bullet\bullet}] + 2[M_i^{\bullet\bullet}] - [e'] = 0 \quad \text{or} \quad 2[v_o^{\bullet\bullet}] + 2[M_i^{\bullet\bullet}] = [e'] \quad (1.2)$$

Despite its simplicity, and despite its use in e.g. traditional aqueous chemistry, the electroneutrality condition tends to cause both conceptual difficulties and occasional errors (by misplacing the coefficients z). In order to help, we suggest that one learns it by heart and uses it accordingly. Moreover, remember that it does *not* keep account of the concentration of species but of the concentration of *charges*. Finally, remember that it is *not* a chemical reaction, but a *mathematical relationship*. It thus does not intend to conserve mass or charge, it simply counts positive and negative charges from whatever concentrations of charged species that are present and requires them to be equal.

Stoichiometry and nonstoichiometry

The compositions and chemical formulae for metal oxides and other inorganic compounds are usually written with a simple ratio of cations to anions, e.g. M_aO_b where a and b are small integers determined by the valence of the constituent atoms. In crystalline compounds this also reflects that the structure contains different types of sites (e.g. close-packed sites and tetrahedral or octahedral interstices) in simple ratios and that these are selectively and systematically filled with cations or anions. When the oxide M_aO_b contains M and O atoms in the exact ratio $a:b$, it is said to have a *stoichiometric* composition.

As mentioned above, an exact stoichiometric composition in inorganic compounds is in principle the exception rather than the rule. Oxides in equilibrium with their surroundings are thus generally *nonstoichiometric*, except under specific conditions of temperature and activities of the components. However, within our experimental ability to measure the ratio of the constituent atoms, many inorganic compounds may be considered to be so near stoichiometry over large temperature and activity ranges that minor deviations from stoichiometry may often be neglected in a discussion of defect concentrations and defect-controlled properties.

Numerous oxides will, however, exhibit marked deviations from stoichiometry. Some oxides are even unstable when stoichiometric. Wustite, for instance, which is nominally written FeO, has under all conditions where it exists, a deficiency of iron which varies with temperature and oxygen activity, and its formula should correspondingly be written $Fe_{1-x}O$. In many systems of the transition metal oxides there exist phases which show large variations from the apparent stoichiometric composition in that the average valences of the metal ions in these phases are intermediate between the integral valences of the metal ions. These arise due to the elimination of defects in the form of shear planes. One often finds homologous series of oxides of this kind, with

small differences in average valence and composition. This will be further discussed below.

In the following is given a qualitative description of different simple defect structures. The corresponding defect equilibria that express the concentration of the different point defects as a function of temperature and oxygen activity are treated in a later chapter.

Defects in stoichiometric compounds.

Let us consider a stoichiometric crystal with composition MX. If a charged point defect is formed in such a crystal, a complementary point defect with opposite effective charge must be formed to conserve the electroneutrality of the stoichiometric crystal. Two types of defect structures involving point defects have been found to be important in stoichiometric metal oxides and these are termed Schottky and Frenkel defects, respectively, honouring early contributions of two of the many German scientists who pioneered the development of defect chemistry (Schottky (1935), Frenkel (1926)).

Schottky disorder

A stoichiometric crystal with Schottky disorder contains equivalent concentrations of cation and anion vacancies. A stoichiometric oxide MO contains equal concentrations of metal and oxide ion vacancies. In a stoichiometric oxide MO_2 the concentration of oxygen vacancies is twice as large as that of the metal ion vacancies. It may be noted that the formation of Schottky defects can only occur at surfaces or other extended defects (like dislocations and grain boundaries) since the atoms in the vacated sites must escape. The defects then diffuse into the crystal until equilibrium is reached.

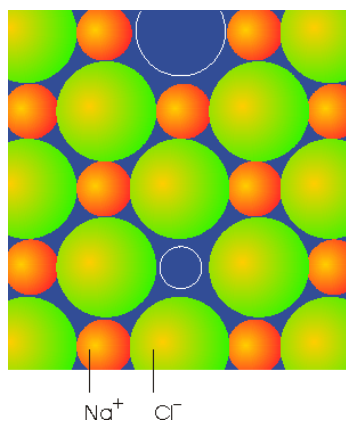


Figure 1-17 Schottky defect pair in NaCl. From Shriver and Atkins (1999).

Frenkel disorder

A stoichiometric crystal with Frenkel disorder contains the same concentrations of metal vacancies and metal interstitial ions. Contrary to the Schottky defects, Frenkel

defect pairs can be formed directly inside the crystal by the atom going directly into interstitial sites from the normal sites without long-range diffusion.

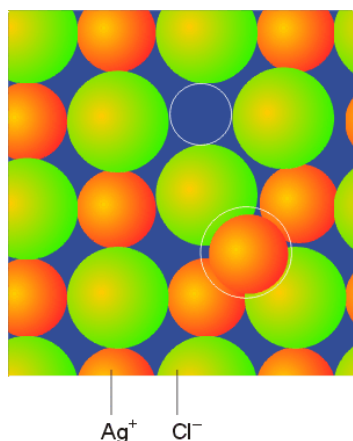


Figure 1-18. Cation Frenkel defect pair in AgCl. From Shriver and Atkins (1999).

Frenkel pairs that consist of anion vacancies and anion interstitials are called anion–Frenkel pairs or sometimes anti-Frenkel pairs.

Although Schottky and Frenkel disorder may be simultaneously present in stoichiometric compounds, one type of disorder usually predominates. As a rule of thumb, Schottky disorder is favoured in crystals where the cations and anions are of comparable size, while Frenkel disorder predominates when the sizes of the cations and anions are appreciably different. Another factor is that Schottky disorder tends to dominate when the structure is very effectively packed so that the interstitials that are part of Frenkel pairs are hard to form.

Pairs of interstitials (cation and anion) can be imagined, but have not been found as a dominant defect structure.

Anti-site disorder (swapping of sites) is common in intermetallics and between cations on different sites (or anions on different sites). However, swapping between cations and anions in ionic compounds is mostly prohibited by the very unfavourable effective charges that would arise.

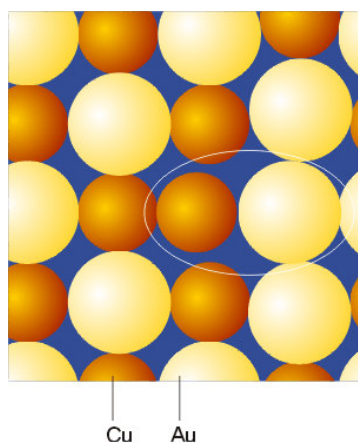


Figure 1-19. Anti-site defect pair in CuAu intermetallic. From Shriver and Atkins (1999).

Defects in nonstoichiometric oxides.

The deviation from the exact stoichiometric composition is directly related to the presence of point defects. While complimentary point defects are formed in stoichiometric crystals, the electrical neutrality of nonstoichiometric compounds is conserved through the formation of point defects and charge compensating electronic defects.

Nonstoichiometric oxides may - depending on the oxide, temperature and activities of the components - have an excess or deficit of metal or oxygen. In view of this, nonstoichiometric oxides may be divided in four limiting groups:

- Metal deficient oxides, e.g. $M_{1-x}O$, where x is usually a small fraction of 1. Metal vacancies are the majority defects. The metal vacancies are compensated by electron holes. Examples of oxides with metal deficit are $Co_{1-x}O$, $Ni_{1-x}O$, and $Fe_{1-x}O$;
- Metal excess oxides, e.g. $M_{1+x}O$, in which metal interstitials are the prevalent defects, compensated by defect electrons. $Cd_{1+x}O$ is an example of an oxide with this type of nonstoichiometry;
- Oxygen deficient oxides, e.g. MO_{2-y} . In these oxides oxygen vacancies compensated by defect electrons prevail, and examples of such oxides are CeO_{2-y} and other oxides with the fluorite structure;
- Oxygen excess oxides, e.g. MO_{2+y} such as, for instance UO_{2+y} . Oxygen interstitials compensated by electron holes are the predominating defects.

Although a particular type of defect predominates in an oxide and as such constitutes the majority defect in the crystal, it is important to emphasise that the crystal will contain all other defects in varying concentrations in the form of minority defects. Furthermore, the majority defects in the crystal may also change with temperature or activity of the components in the crystal. By way of example, in an oxide MO_2 the predominant defects may in principle change from oxygen vacancies to interstitial metal ions on changing the oxygen activity, and under these conditions the nonstoichiometry may be written $M_{1+x}O_{2-y}$.

More complex defects

Point defects are often assumed to be present as single, unassociated point defects that are randomly distributed in the structure. However this is in principle only applicable for small defect concentrations, that is, typically when the fraction of defects (relative to the number of normal atoms in the crystal) is smaller than 0.001-0.01 (but depending a lot on temperature).

For larger defect concentrations one expects that defects begin to interact. The interactions can be coulombic or elastic (related to space and size). They can be attractive or repulsive. These interactions may change the activity coefficients and formation enthalpies of defects, and they may lead to associations between defects which attract each other. A simple example is the association of a native point defect and a dopant or impurity ion with opposite effective charges. Energy minimisation may for large defect concentrations lead to clusters of different defects. It may also lead to accumulation of many of the same defect in lines or planes. If the defects or lines or planes order in a systematic repeating manner, we have obtained a new structure. Elimination of planes is called shear structures, because building blocks that used to be separate now shear lattice points.

Order or disorder of defects is a matter of a fine balance between the configurational entropy of the defects and the exothermic enthalpy gained in association of certain point defects to form various types of larger defect agglomerations. Systems with relatively small defect concentrations are entropy controlled and consist of randomly distributed point defects. As concentration increases the enthalpy takes control and leads successively to formation of larger defect entities; randomised associated defects or defect clusters, point defects assimilated into randomised structure elements of a new phase, superlattice ordering and extended defects, shear planes, and discrete intermediate phases.

From simple thermodynamics, increasing temperature favors entropy, and at sufficiently high temperatures disorder and simple defects will dominate. At sufficiently low temperatures, enthalpy and the more complex defects take over.

It may be noted, however, that extended defects like dislocations and grain boundaries are never thermodynamically stable. While point defects or clusters may form spontaneously from the perfect crystal because of entropy, extended defects do not produce enough entropy for this. They will thus not form from a perfect crystal; they are metastable remains of the fabrication of the solid.

Example cases of defect clusters

Defect clusters in a metal-deficient oxide: $Fe_{1-x}O$

A well known example of an oxide where the point defects form defect clusters is wustite, $Fe_{1-x}O$. As mentioned above, under normal equilibrium conditions the oxide is never stoichiometric; the value of x ranges from 0.05 to 0.15 depending on the temperature and oxygen activity. Following the composition of the oxide it was originally believed the point defects were iron vacancies. However, extensive structural investigations by X-ray, electron and neutron diffraction have over the years shown that the defects not only comprise Fe-vacancies but also Fe-interstitials. The earliest studies of complexes indicated that for each vacancy created as a result of nonstoichiometry, a Frenkel defect pair was also formed. The combination of these defects gave a complex defect consisting of an interstitial ion (on a tetrahedral site) adjoined by two vacancies (vacant octahedral sites). Further studies have shown that the complexes comprise combinations of larger number of vacancies and interstitials with ratios of vacancies to interstitials ranging from 3 to 4. The basic unit of such clusters consists of four

vacancies and one interstitial. Such units may further combine to form more complex clusters through side-, edge-, and corner-sharing and for these the ratios of vacancies to interstitials are close to 3. It is noteworthy that the larger corner-sharing clusters have the same local atomic arrangement as magnetite, Fe_3O_4 , and these can be considered as nuclei of Fe_3O_4 to which Fe_{1-x}O transforms when the defect concentrations exceed critical values. The defect cluster in question might be denoted $(4v_{\text{Fe}}\text{Fe}_i)^{6'}$.

Defect clusters in an oxide with excess oxygen: UO_{2+y}

Uranium dioxide has the fluorite structure and may have a deficit or excess of oxygen depending on the temperature and oxygen activity. Under conditions when it has excess oxygen, UO_{2+y} , the maximum value that y may have is 0.25. This composition may suggest that the predominant point defects are oxygen interstitials, however, as shown by Willis through neutron diffraction studies the defects are not single unassociated oxygen interstitials, but comprise clusters of oxygen interstitials and vacancies. The real composition of the clusters and detailed location of the individual point defects in the clusters are still a matter of discussion, but the formation of clusters may qualitatively be visualised as follows: When an oxygen atom is dissolved interstitially an oxygen atom on a neighbouring normal site is simultaneously displaced to neighbouring interstitial site leaving behind a vacant normal oxygen site. This qualitative model suggests a defect cluster consisting of two oxygen interstitials and an oxygen vacancy. Later studies have shown that clusters consist of larger number of oxygen interstitials and vacancies.

Shear structures.

Extended defects are planar defects and may be considered to be formed by ordering and elimination of point defects, e.g of oxygen vacancies, along specific crystallographic planes. The process is illustrated for WO_{3-y} below. The predominant defects are in this case assumed to be oxygen vacancies and are considered to be aligned as illustrated. By shear of these crystals the aligned vacancies are eliminated, and this produces a fault in the cation sublattice. The formation of shear phases gives rise to the homologous series of oxide structures, e.g $\text{W}_n\text{O}_{3n-1}$ and $\text{Ti}_n\text{O}_{2n-1}$. In this way the crystals may be able to have variable composition and may as such be termed nonstoichiometric.

The schematic depictions of defective structures shown initially in this chapter contain some other extended defects, like dislocations, aggregates and precipitates. Contrary to point defects, extended defects can often be imaged directly in electron microscopy, as seen in the figure below.

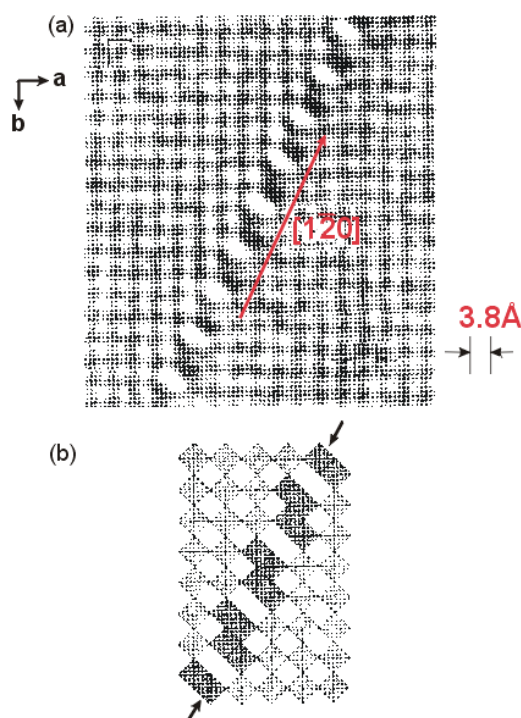


Figure 1-20. Real and simulated image of shear plane in WO_{3-y} . From Shriver and Atkins (1999)..

Modulated structures/ininitely adaptive structures

A few oxide systems and other compounds may accommodate nonstoichiometry by continuous adjustment of a parent structure without forming point defects. Such structures are now called modulated nonstoichiometric compounds, but these have also in the literature been termed vernier structures or infinitely adaptive structures. An example of such an oxide is the low-temperature modification of tantalum pentoxide, $L\text{-Ta}_2\text{O}_5$. The oxide exchanges oxygen with the ambient atmosphere, but the monophasic structure is maintained through the creation or elimination of oxygen sites in the oxygen sublattice while the number of tantalum sites remains unchanged.

Summary

Due mainly to the gain in enthalpy of electrostatic attractions and electron orbital overlap, solids usually organise their constituent ions, atoms, or molecules in a crystal lattice. In such lattices the species take specific positions relative to each other, and this pattern is repeated in 1, 2 or 3 dimensions. Different compounds take on different geometrical arrangements depending on the properties of the constituents. This is a complex function of the charge distribution of each atom or ion, in turn a function of nuclear charge, ionisation energies, electron affinity and shape of the valence electron orbitals. However, it is often useful to view the structures as close-packing or other

packings of rigid spheres, with systematic filling by smaller spheres of voids so created. Because of the preferred occupation of specific sites in the lattice, together with the tendency of distinct preferences in valence for the various elements, most compounds are basically stoichiometric, that is, the ratio of the different atoms is a simple ratio of small integers. Moreover, most solid compounds have enough valence electrons to fill up the bonding orbitals and form a filled electron energy valence band, with an empty band gap to the next, empty band, the conduction band. (Exceptions are metals, with partially filled bands.) In competition with this minimisation of enthalpy with perfect, stoichiometric lattices and filled and empty bands, we have the tendency of increasing the entropy at $T > 0$ K by the creation of defects. At any temperature there is thus an equilibrium concentration of defects. The defects comprise point defects (vacancies, interstitials and substitution), electronic defects (conduction electrons, holes, valence defects), and associates, clusters, lines or planes of defects. A point defect is denoted in Kröger-Vink notation by its constituent (a chemical element symbol or a vacancy (v)), a subscript indicating lattice site or interstitial site (i) and a superscript indicating effective positive or negative charges (\cdot or $/'$). We have learned to set up the electroneutrality condition using effective charges.

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Problems

1. If English is not your first or native language, try to translate the defect names used in Figure 1-1 and Figure 1-2 from English into your first language.
2. Calculate the number of atoms in the bcc and sc unit cells of Figure 1-10 and Figure 1-11. (If you are not familiar with the procedures: Count all atoms, but divide by 2, 4, or 8 for atoms that are shared with neighbouring cells by being in faces, edges or corners.)
3. Calculate the number of atoms in the hcp and fcc unit cells of Figure 1-7.
4. Calculate the number of ions of each kind in the NaCl and ABX_3 cells in Figure 1-12 and Figure 1-15.
5. Calculate the number of atoms and voids in the cells in Fig. 1-6.
6. Calculate the volume filling ratio of spheres in the structures of Figure 1-7 b), Figure 1-10, and Figure 1-11. What would it be in Figure 1-7 a)?
7. Why would you say metals generally feel heavier (have higher densities) than ionic compounds (salts and ceramics)?
8. Sketch the periodic table of the elements, but include where possible the typical binary oxides of the elements in their normal (most common) oxidation states, in terms of formulae (stoichiometry) and structure type. Indicate also, based on what you know about their tendency to take on neighbouring oxidation states, whether the oxide is expected to be stoichiometric, have oxygen-deficiency, or oxygen-excess.
9. List the main types of 0-, 1-, 2-, and 3-dimensional defects in crystalline solids.
10. Write the Kröger-Vink notation for the following fully charged species in MgO: Cation and anion on their normal sites, oxygen vacancy, magnesium vacancy, interstitial magnesium ion.
11. Write the Kröger-Vink notation for the following species in ZrO_2 : Cation and anion on their normal sites, oxygen vacancy, zirconium vacancy, yttrium dopant substituting Zr, interstitial carbon atom, cluster of yttrium dopant and oxygen vacancy, nitrogen ion (N^{3-}) substituting for oxide ion.
12. Write the Kröger-Vink notation for the following fully charged species in $CaTiO_3$: Calcium vacancies, titanium vacancies, oxygen vacancies, Ti ions on Ca sites and vice versa, Ti interstitials.
13. For the materials and list of defects in Exercises 10-12, write the electroneutrality conditions.
14. Suggest a simplified electroneutrality condition for the two dominating defects in Y-doped ZrO_2 .
15. Write the electroneutrality condition for defects in boron-doped silicon.
16. Write the electroneutrality condition for defects in phosphorous-doped silicon.
17. Write the electroneutrality condition for pure (undoped) silicon.

1. Bonding, structure, and defects

18. Write an electroneutrality condition for MO_{1-y} (hint: includes two defects: a point defect and an electronic defect).
19. Write an electroneutrality condition for MO_{1+y} .
20. Write an electroneutrality condition for M_{1-x}O .
21. Write an electroneutrality condition for M_{1+x}O .
22. Write in Kröger-Vink notation the most probable species and defects in a material of your choice – preferably a compound you are working with or are going to work with. Include both positive and negative defects. Then set up the electroneutrality condition including all defects. Finally, make a guess of the most important positive and the most important negative defect, assuming that the concentrations of the remaining are negligible, and set up the simplified limiting electroneutrality condition.

Answers and hints to selected Problems, Ch. 1

1. E.g. Norwegian: vakans (eller tomlass); interstitell (eller mellomgitterplass);
....
2. 2, 1
3. 6, 4
4. 4:4, 1:1:3
5. 4:4, 4:8
6. 1-4b: $\frac{\pi}{3\sqrt{2}}=0.74$, 1-7: $\frac{\pi\sqrt{3}}{8}=0.68$, 1-8: _____, 1-4a: $\frac{\pi}{3\sqrt{2}}=0.74$.
7. Search the text...
8. -
9. Search the text...
10. Mg_{Mg}^x O_{O}^x $\text{v}_{\text{O}}^{\bullet\bullet}$ $\text{v}_{\text{Mg}}^{\prime\prime}$ $\text{Mg}_{\text{i}}^{\bullet\bullet}$
11. Zr_{Zr}^x O_{O}^x $\text{v}_{\text{Zr}}^{\prime\prime\prime}$ or $\text{v}_{\text{Zr}}^{\prime\prime\prime\prime}$ $\text{Y}_{\text{Zr}}^{\prime}$ C_{i}^x $\text{N}_{\text{O}}^{\prime}$ $(\text{Y}_{\text{Zr}}\text{v}_{\text{O}})^{\bullet}$
12. -
13. Exc. 10: $2[\text{v}_{\text{O}}^{\bullet\bullet}] + 2[\text{Mg}_{\text{i}}^{\bullet\bullet}] = 2[\text{v}_{\text{Mg}}^{\prime\prime}]$
etc...
14. $2[\text{v}_{\text{O}}^{\bullet\bullet}] = [\text{Y}_{\text{Zr}}^{\prime}]$
15. $[\text{B}_{\text{Si}}^{\prime}] = [\text{h}^{\bullet}]$
16. similar...
17. -
18. $2[\text{v}_{\text{O}}^{\bullet\bullet}] = [\text{e}^{\prime}]$
19. similar...
20. -
21. -
22. -