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Defects and Transport in Crystalline Solids

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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 comprehensive reviews of defect structure and defect-related properties of all binary oxides, as known at that time.

The book followed Kofstad's equally well-recognized book "High temperature oxidation of metals" from 1967. The latter was revised and published under the title "High temperature corrosion" in 1987.

In the 25 years that have 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 with a higher degree of sophistication in the models used. Simplifications and approximations are necessary to a lesser extent. Although this development is welcome and unavoidable it brings about a few problems: The sound overview and ability to analyse a situation may be obscured or lost, the newcomer may find the field difficult or unattractive to enter, and there is an increasing chance of overinterpretation of details originating from experimental error.

Along with the development in the application of theory and modelling, the field has changed focus from binary oxides to ternary or higher oxides, much due to the growing awareness that perovskite and related structures tolerate very large substitutions and variations in valence and stoichiometry. 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 barium indate and doped lanthanum gallate, mixed conductors such as the new $Sr_4Fe_{6-x}Co_xO_{13-\delta}$, 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 late 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 force, he was unable to see the book through. I became engaged as a co-author and made a promise to take over and see it through.

I used the new text as a curriculum in my teaching of Kofstad's course in defect chemistry at the University of Oslo, and thereby improved it step by step. However, the burdens of taking over the research group kept me from finishing the book. Furthermore, a textbook on defect chemistry by Kofstad's close friend and colleague, Donald M. Smyth was published that took away some of the immediate need for our textbook. All in all I 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, January 2004

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1. Structure and defects

Introduction

Classical chemistry and crystallography gave an idealised picture of the composition and crystal structure of inorganic compounds. 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 lattice sites will be empty (vacant) and extra atoms may occupy the interstitial space between the atoms on the lattice sites. The empty lattice sites are termed vacancies and the extra atoms interstitial atoms. Following Wagner and Schottky all crystalline solids will at any temperature 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 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, the imperfection is termed a point defect. Vacancies and interstitial atoms are point defects. An impurity atom present in a crystal and that either occupies a lattice 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 are dislocations which are characterised by displacements in the structure in certain directions. The plane defects comprise stacking faults, grain boundaries, internal and external surfaces.

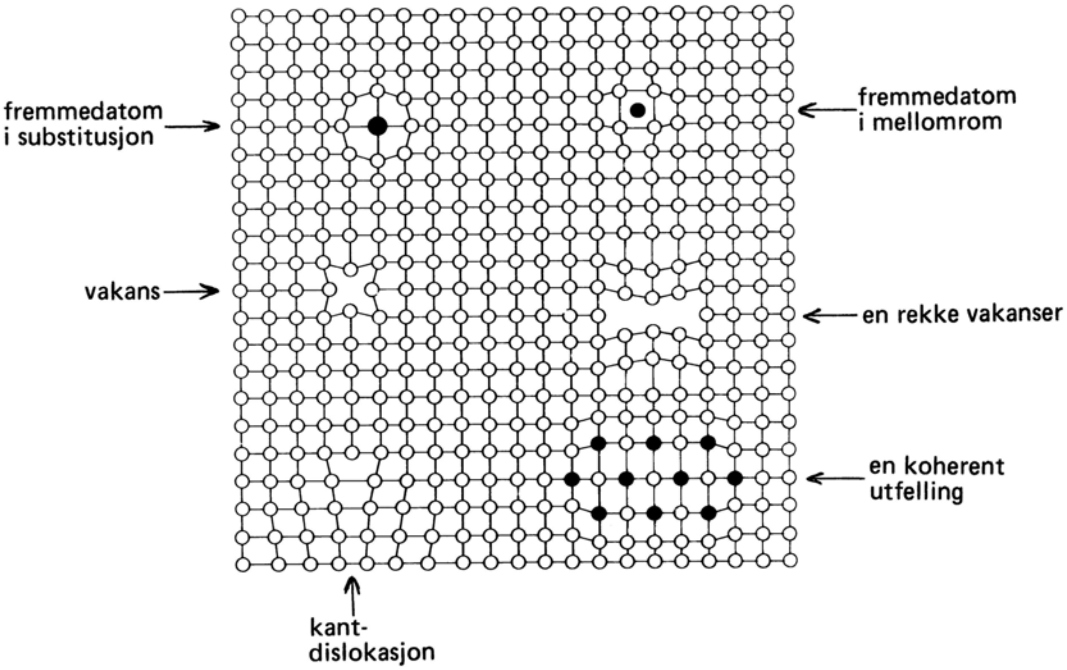


Figure 1-1. Schematic representation of some defects in an elemental solid. From A. Almar-Næss: Metalliske materialer.

In addition to the structural defects, crystals also contain electronic defects, i.e. 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, the electronic defects 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 materials coloured, and composite defects involving point defects and trapped electronic defects are 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 or ionic conductivity in crystalline solids takes 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 is closely related to the defect chemistry of catalysts.

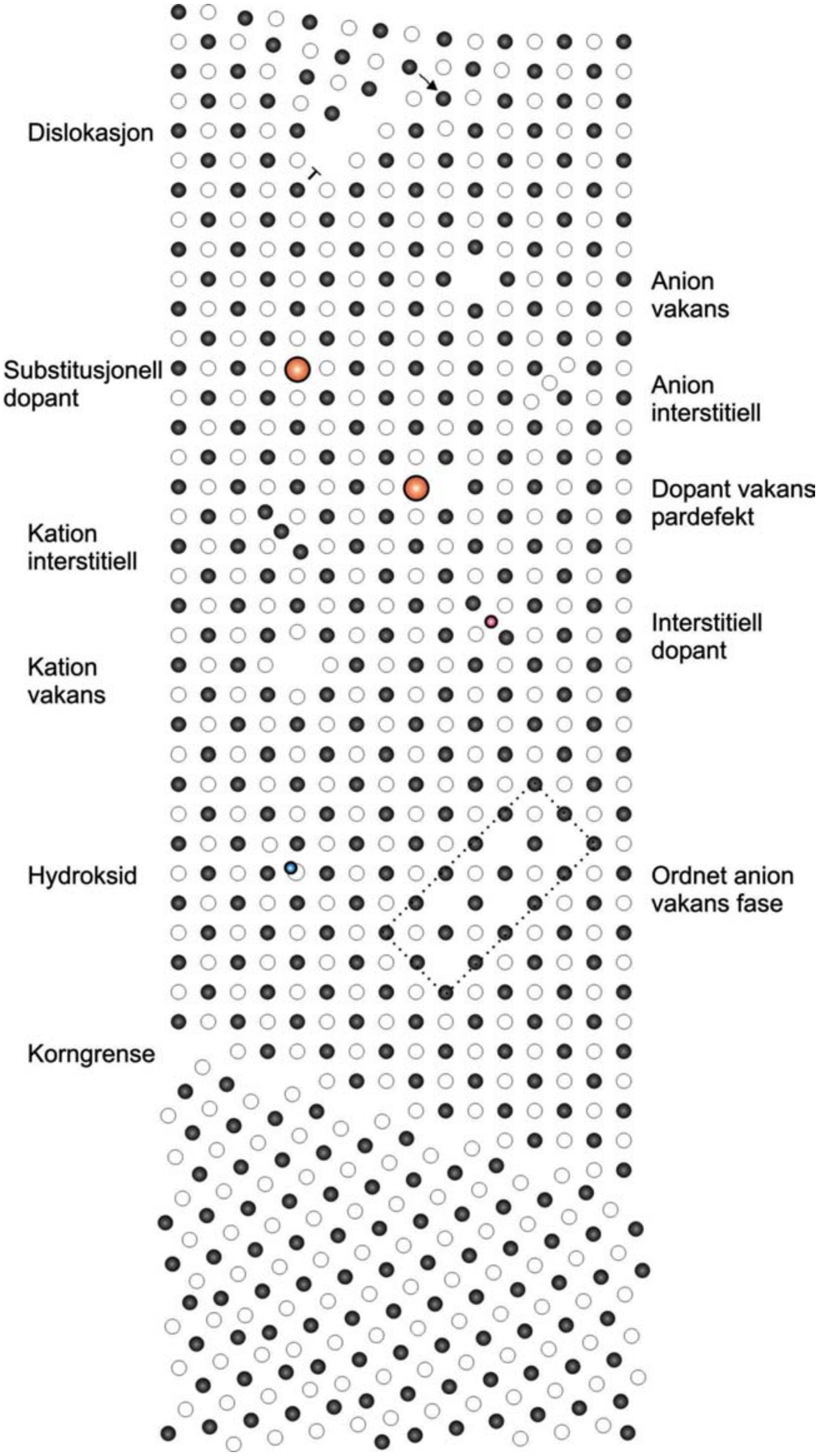

Dislokasjon
Anion vakans
Substitusjonell dopant
Anion interstitiell
Dopant vakans pardefekt
Kation interstitiell
Interstitiell dopant
Kation vakans
Hydroksid
Ordnet anion vakans fase
Korngrense

Figure 1-2. Schematic representation of some defects in an ionic binary compound.

As a basis for further considerations of defect structures and defect-dependent properties to be discussed later in the book, 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.

Common crystal structures

Close-packing and voids

The crystal structures of many metals 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 oxygen 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. 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 ABABAB... as illustrated in (a) of the figure below. This type of close-packed stacking is called hexagonal close packing (hcp) of the spheres because it gives crystal structures with hexagonal symmetry.

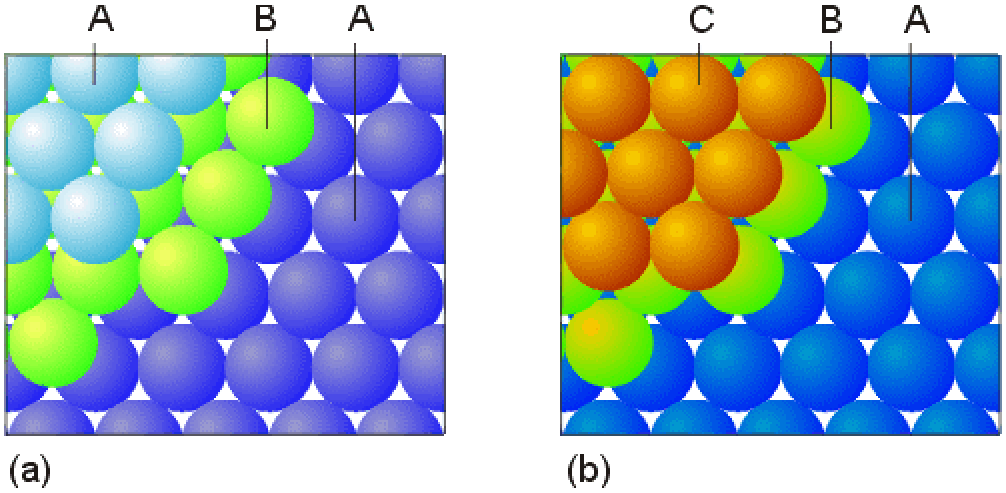


Figure 1-3. ABABAB…(hcp) clos-packing (a) and ABCABC…(fcc) close-packing (b) of spheres. From Shriver and Atkins; Inorganic Chemistry.

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 (b) in the figure above. The stacking sequence is now ABCABC... and this close packing is known as cubic close packing (ccp) as this gives rise to a cubic (face-centred) crystal structure. The following figure shows how the two close-packed structures appear when their heaxonal and face-centred cubic unit cells are emphasized.

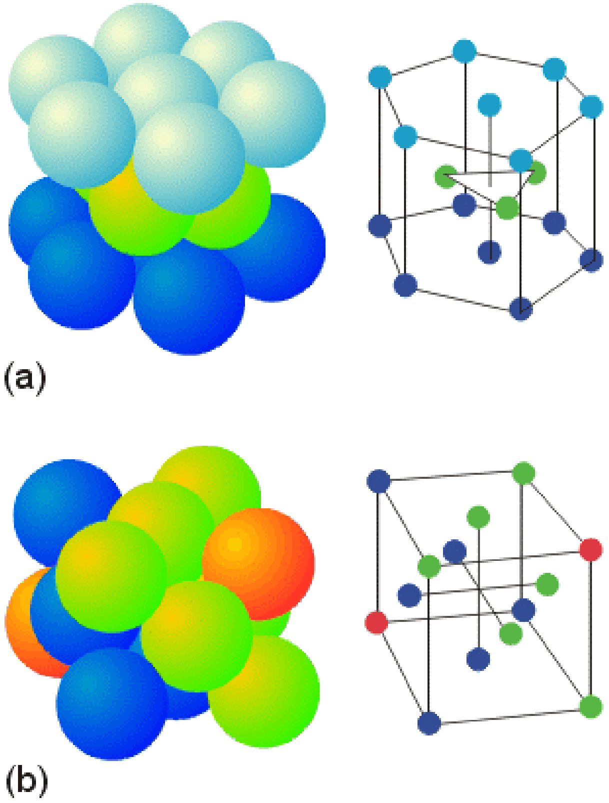
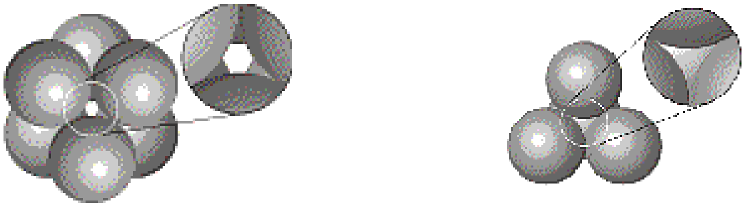


Figure 1-4. Schematic views of the hcp (a) and fcc (b) structure types. From Shriver and Atkins; Inorganic Chemistry.

The close-packed structures contain two different types of empty space or voids between the spheres, cf. the figures below. One type of void is termed a tetrahedral void because each of these voids is surrounded by four spheres which centres are at the corners of a tetrahedron. The other 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. 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. In different 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 interstices in regular patterns.



2 Octahedral hole 5 Tetrahedral hole

Figure 1-5. Octahedral and tetrahedral hole in close-packed layers of speheres. From Shriver and Atkins: Inorganic Chemistry.

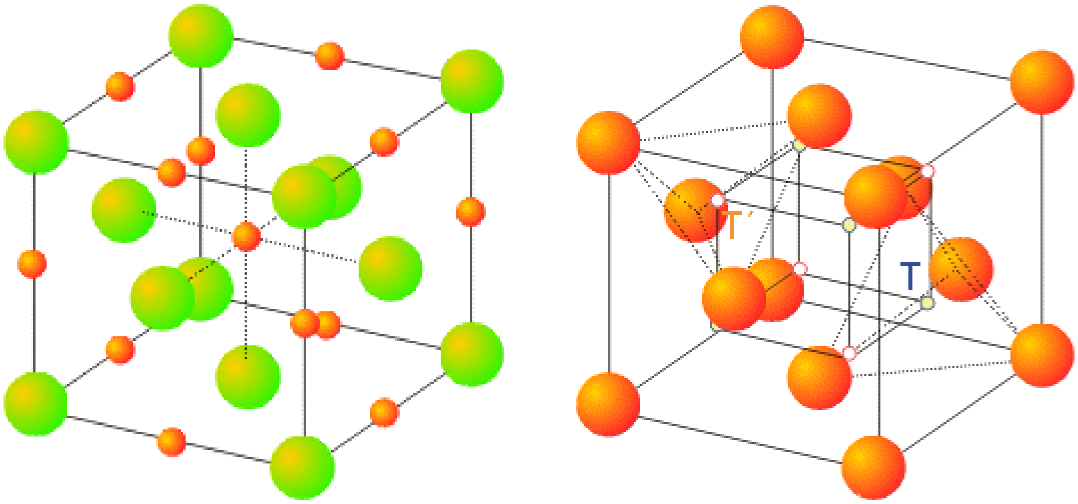


Figure 1-6. Small spheres show locations of octahedral (left) and tetrahedral (right) voids in fcc structure. From Shriver and Atkins: Inorganic chemistry.

Less close-packed arrangements

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

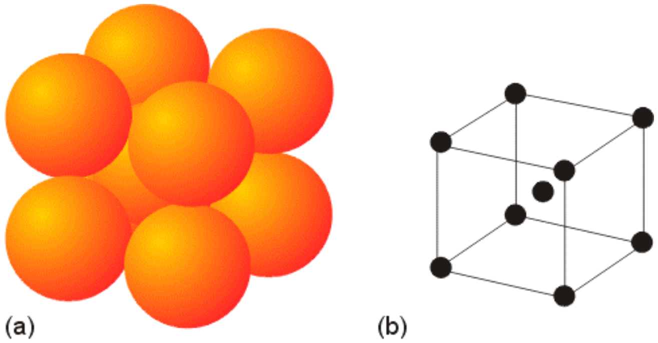


Figure 1-7. Body-centered cubic (bcc) packing of spheres. From Shriver and Atkins: Inorganic Chemistry.

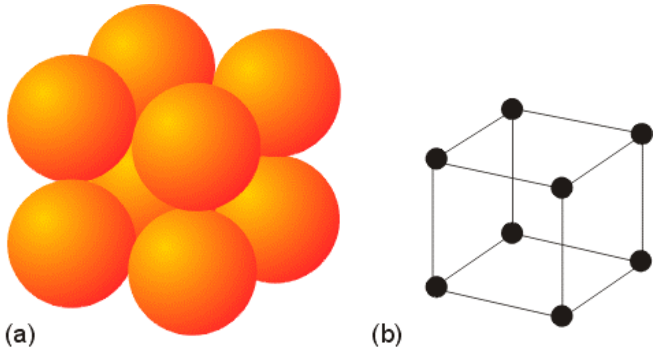


Figure 1-8. Simple cubic (sc) packing of spheres. From Shriver and Atkins: Inorganic Chemistry.

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. (Note that once the structure is established, the interstices occupied by 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 than their neutral atoms and positively charged ions (cations) are much smaller than their neutral atoms.

One may also recall that the effective size increases with the coordination number.

In the following we look at some example structures possessed by oxides.

The NaCl (rock salt, halite) structure

In the NaCl structure the anions are cubic close-packed, 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.

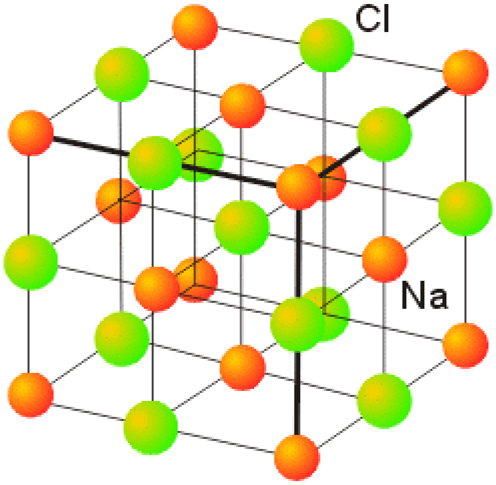


Figure 1-9. The NaCl structure. Note that the centre anion is six-coordinated, as are also all other ions.

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 structures highly defective.

In the sulfides FeS and NiS, the structure is similar, but the close-packing of anions is hexagonal 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 CaF_2 (fluorite) structure

The fluorite structure is named after the mineral calcium fluoride (CaF_2) and is illustrated below. This structure may geometrically be considered to constitute a close-packing of the metal ions while the anions occupy all the tetrahedral sites. The calcium ions are smaller than the fluoride ions and the fluoride ions are thus not able to fit into the interstices of the calcium ion array, but the model describes the relative positions of the ions. It is nevertheless more correct to view the structure as a simple cubic packing of anions (not close-packed), with cations filling every second cubic void, as also depicted below; each cation is surrounded by eight anions.

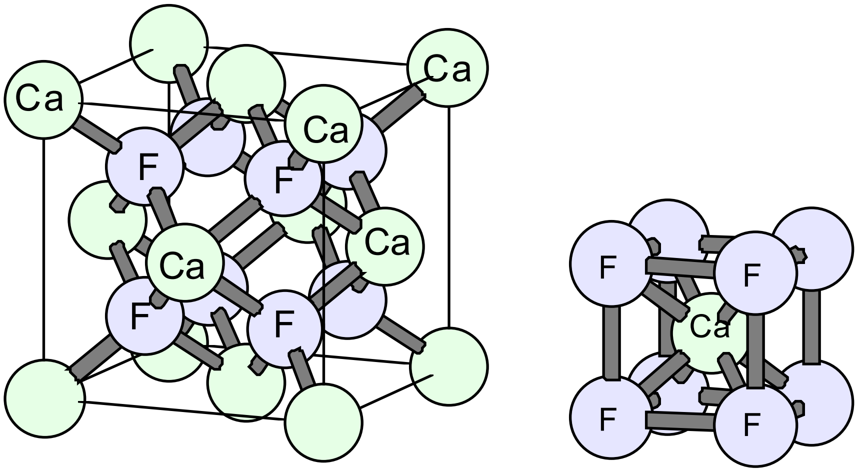


Figure 1-10. The CaF_2 structure shown as fcc-packed cations with anions in all tetrahedral voids (left) and simple cubic packing of anions with cations in every other cubic voids (right).

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. The oxides ZrO_2, HfO_2, CeO_2, ThO_2, PuO_2, etc. possess the fluorite structure. All the octahedral interstices 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 ($ABO_{3.5}$) and C-type rare earth sesquioxide (A_2O_3) structures can be viewed as fluorite with, respectively, 1/8 or 1/4 of the oxygen 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 oxygen ions can be considered to be cubic close-packed (fcc) while the metal ions occupy all the tetrahedral sites.

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 hcp packing of the oxygen ions, while Ti ions occupy 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 is tetrahedral, and when the structure is viewed along the c-axis it may be seen that the structure contains channels in the c-direction.

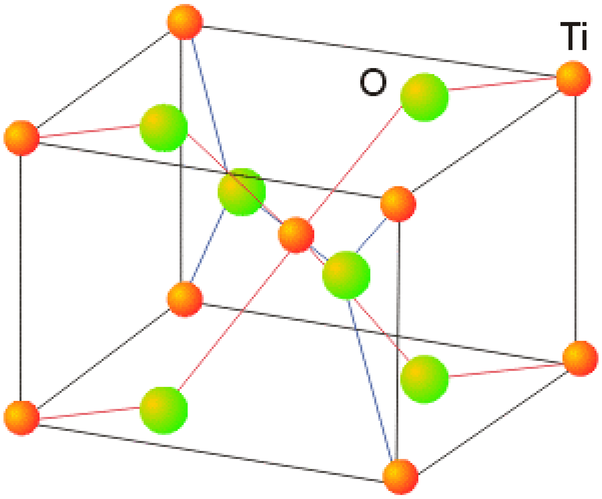


Figure 1-11. The rutile TiO_2 structure. From Shriver and Atkins: Inorganic chemistry.

In addition to rutile itself, the oxides SnO_2, MnO_2, VO_2, MoO_2, RuO_2, GeO_2 a.o. possess regular or distorted rutile structures.

The corundum (α-Al_2O_3) and ilmenite ($FeTiO_3$) structures

The corundum structure is named after the high temperature modification of alumina, α-Al_2O_3. This structure may be described as a hexagonal close-packing (hcp) of oxygen ions with the trivalent aluminium ions occupying 2/3 of the octahedral sites. As the metal ions occupy octahedral sites, each metal ion is octahedrally coordinated and surrounded by six oxygen atoms, while each oxygen atom is surrounded by four metal ions, see Figure below. Two and two metal ions occupy neighbouring interstitial octahedral sites, and the two corresponding AlO_6 octahedra are linked by common faces. Other oxides possessing the corundum structure are α-Fe_2O_3, Cr_2O_3, Ti_2O_3, and V_2O_3. A number of oxides with the nominal formula $ABO3$ may have the corundum type structure when the metal ions A and B have an average valence of 3 and are of approximately the same size.

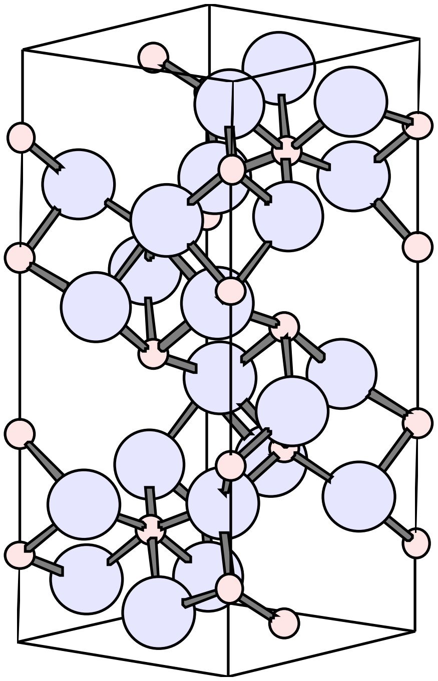


Figure 1-12. The corundum (α-Al_2O_3) structure. One may observe the octahedral coordination of Al ions and the seemingly complex filling of Al ions in the voids. Note that the structure comprises a fully close-packed hcp arrangement of oxygen ions, while the figure may give the impression of a rather open packing.

The ilmenite structure with the nominal formula ABO_3 and named after the mineral $Fe^{II}Ti^{IV}O_3$ is similar to the corundum structure in that the oxygen 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 is trivalent, B^{3+}. In the spinel structure the oxygen 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, as illustrated in Figure 1.7. The unit cell contains 32 octahedral and 64 tetrahedral sites. In the normal spinel structure one half of the octahedral sites are occupied by the B^{3+}-ion while the A^{2+} ions occupy 1/8 of the tetrahedral sites.

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 $Fe(MgFe)O_4$.

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 atoms and the oxygen atoms together form a close-packed lattice, such that each A-atom is coordinated to twelve oxygen atoms. The B-atoms occupy octahedral sites surrounded by six oxygen ions. 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).

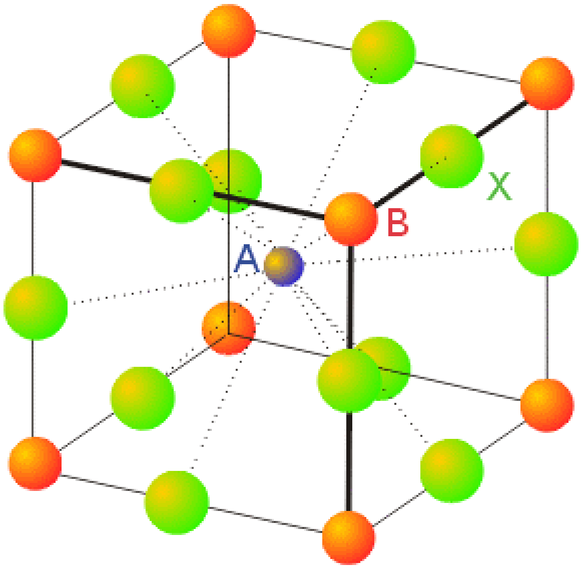


Figure 1-13. Perovskite ABX_3 structure showing the 12-coordination of the A cation. (The A cation is depicted small, but is in reality much bigger than the B cation. From Shriver and Atkins: Inorganic chemistry.

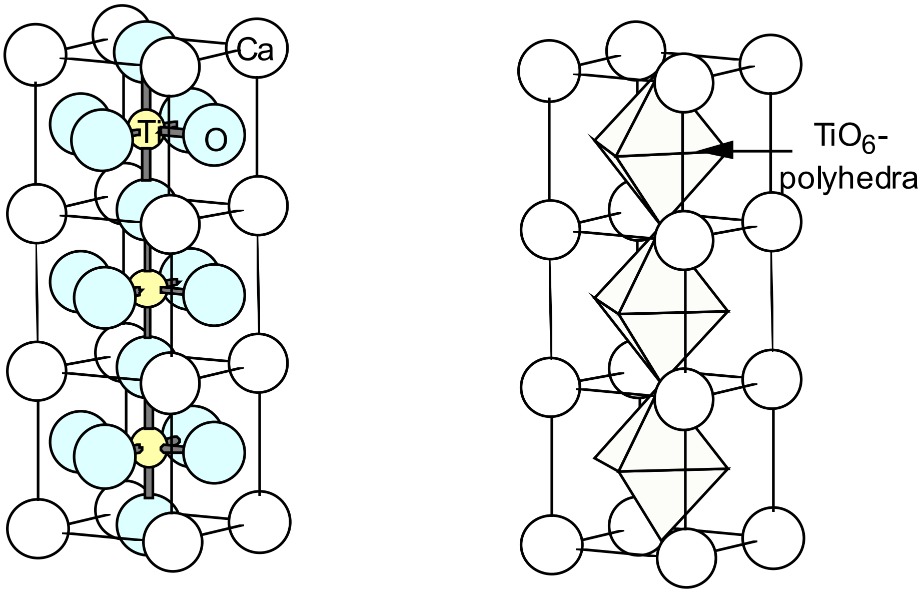


Figure 1-14. Three unit cells of $CaTiO_3$ perovskite structure, represented with atoms on the left and the same structure with octahedra representing the TiO_6 units on the right.

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 ordered intermediate phases.

Summary of relations between structures, cation radii and anion packing arrangements.

In oxides with small cations only, the structure is dominated by close-packing of the oxygen ions and various occupancies of interstices 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 oxygen ion sublattices.

Formula	Cation:anion coordination	Type and number of occupied interstices	fcc of anions	hcp of anions
MO	6:6	1/1 of octahedral sites	NaCl, MgO, CaO, CoO, NiO, FeO a.o.	FeS, NiS
MO	4:4	1/2 of tetrahedral sites	Zinc blende: ZnS	Wurtzite: ZnS, BeO, ZnO
M_2O	8:4	1/1 of tetrahedral sites occupied	Anti-fluorite: Li_2O, Na_2O a.o.	
M_2O_3, ABO_3	6:4	2/3 of octahedral sites		Corundum: Al_2O_3, Fe_2O_3, Cr_2O_3 a.o. Ilmenite: $FeTiO_3$
MO_2	6:3	½ of octahedral sites		Rutile: TiO_2, SnO_2
AB_2O_4		1/8 of tetrahedral and 1/2 of octahedral sites	Spinel: $MgAl_2O_4$ Inverse spinel: Fe_3O_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.

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 Náray-Szabó (1969) and Rao and Raveau (1995).

Point defects

In order to understand and describe properties of inorganic compounds 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, first of all, requires a system of notation to describe the point defects and the constituent atoms of the inorganic compounds and their charges.

Notation for description of point defects

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 an imperfection is indicated by a major symbol describing its chemical content and a subscript that indicates the site that it occupies.

In an oxide the metal ions on the regular lattice positions are written M_M, where the subscript thus describes the type of lattice site which is occupied. Correspondingly, the oxygen ions on normal lattice sites are written O_O.

The native point defects in an oxide include M and O vacancies and M and O interstitial atoms or ions. Vacancies are denoted by v with a subscript M or O referring to vacant metal or oxygen sites, respectively. Interstitial ions or sites are described with a subscript "i". Vacancies and interstitials in an oxide are thus written

v_O oxygen vacancy,

v_M metal vacancy,

O_i oxygen interstitial,

M_i metal interstitial.

Correspondingly, an unoccupied or vacant interstitial site can be written v_i.

While the notation traditionally has used V for vacancy, confusion with the element vanadium (V) can be avoided by using lower-case v or italic *V*. Here, we will use the lower case v.

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 cation site is similarly written O_M, but is an example of a very unstable defect.

Real crystals always contain impurities. When a foreign metal ion Mf occupies a regular M site, the foreign atom is denoted by Mf_M. If it occupies an interstitial site, it is described by Mf_i.

Notations for other or more complex defects will be introduced when needed.

Notation for charged defects

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.

In the following, oxygen ions on regular sites in an oxide will be considered to have a formal valence of -2. The cations have a positive charge so as to make the sum of all positive and negative charges in the compound equal to zero.

The point defects may be neutral or charged. Their charges may be described in terms of their 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 oxygen 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 may 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.

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 supscript dot ($^\bullet$) and the effective negative charge by a superscript prime ($^/$). Singly and doubly charged oxygen vacancies are, for instance, 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 oxygen 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. Common examples are found in the semiconductor field. Boron dissolved in silicon is denoted B_{Si}^{x} in the unexcited state, where we have B^0. 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 and becomes B^- or, in Kröger-Vink notation, $B_{Si}^{/}$. Boron is 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}^{x}.

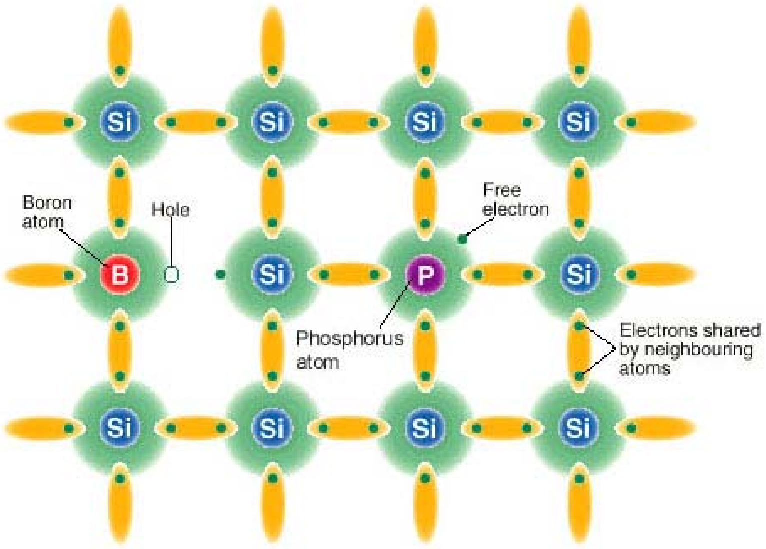


Figure 1-15. Schematic view of electronic structure of boron- and phosphorous-doped silicon. From http://acre.murdoch.edu.au/refiles/pv/text.html

Defect electrons and electron holes 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 $M_M^{/}$.

We have mentioned but a few types of defects to illustrate the principles of notation. Many other defects can be described in the same way; we will see more defects later on.

In addition to the notation, the important thing to remember about charges is the following: *The effective charge of a species is the real charge of the species minus the real charge the perfect reference lattice would have had in the same volume element.*

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:

$$\Sigma \text{ positive real charges} = \Sigma \text{ negative real charges}$$

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:

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

This principle of electroneutrality forms one of the basic equations and conditions for treating defect equilibria and for evaluating defect concentrations in crystals. This will be further discussed and used in the next chapter.

It is important to note that the number of positive and negative charges must be compared on equal bases; one may use numbers or concentrations (numbers or moles per unit volume). However, one may in general not use site fractions since the concentrations of different types of sites are not necessarily equal.

Stoichiometry and nonstoichiometry

The compositions and chemical formulae for metal oxides and other inorganic compounds are usually written with a definite ratio of cations to anions, e.g. M_aO_b where a and b are usually 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 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 exhibit marked deviations from stoichiometry. Some oxides are even unstable when stoichiometric. Wustite, for instance, which is nominally written FeO, has under all conditions a deficiency of iron which varies with temperature and oxygen activity, and its formula should correspondingly be written $Fe_{1-y}O$. 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 defect structure situations. 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.

Point defects and defect structures in stoichiometric compounds.

Let us consider a stoichiometric crystal with composition MX. If a charged point defect is formed in such a crystal, a complimentary point defect with opposite effective charge must be formed to conserve the electroneutrality of the stoichiometric crystal. Two types of defect structures 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 oxygen 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 outer and inner surfaces or dislocations and will diffuse into the crystal until equilibrium is reached.

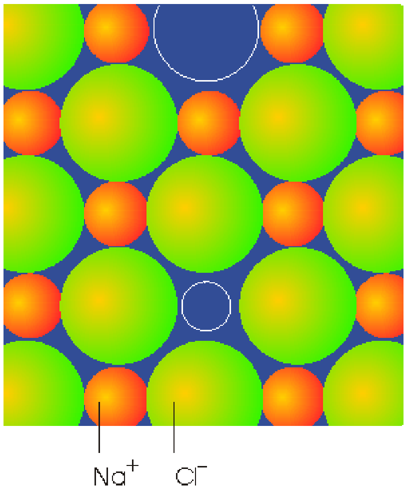


Figure 1-16 Schottky defect pair in NaCl. From Shriver and Atkins: Inorganic Chemistry.

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.

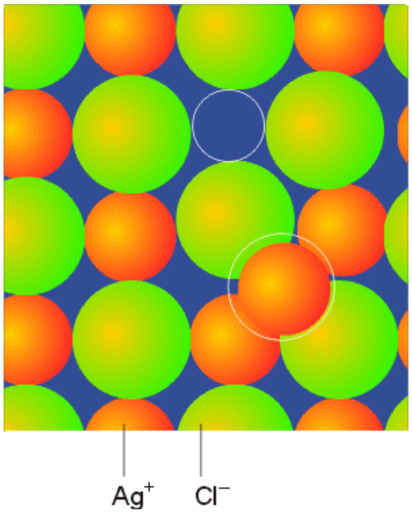


Figure 1-17. Cation Frenkel defect pair in AgCl. From Shriver and Atkins: Inorganic Chemistry.

Although Schottky and Frenkel disorder may be simultaneously present in stoichiometric compounds, one type of disorder usually predominates. As a rough rule 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 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.

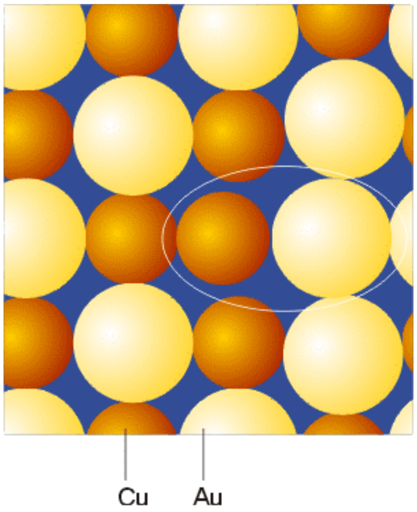


Figure 1-18. Anti-site defect pair in CuAu intermetallic. From Shriver and Atkins: Inorganic Chemistry.

Point defects and defect structures 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 complimentary 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. $M_{1-y}O$, where y is usually a small fraction of 1. Metal vacancies or complex defects based on metal vacancies are the majority defects, and examples with oxides with metal deficit are $Co_{1-y}O$, $Ni_{1-y}O$, and $Fe_{1-y}O$;

- metal excess oxides, e.g. $M_{1+y}O$, in which metal interstitials are the prevalent defects. $Cd_{1+y}O$ is an example of an oxide with this type of nonstoichiometry;

- oxygen deficient oxides, e.g. MO_{2-y}. In these oxides oxygen vacancies 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 or complex defects based on these 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 $M_{1+x}O_{2-x}$.

Associations of point defects, point defect clusters, extended 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 mechanical and 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 or elimination of defects in lines or planes, so as to form a new structure (e.g. shear structures).

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.

Example cases of defect clusters

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

A well known example of an oxide where the point defects form defect clusters is wustite, $Fe_{1-y}O$. As mentioned above, under normal equilibrium conditions the oxide is never stoichiometric; the value of y 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 as illustrated below. 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 $Fe_{1-y}O$ transforms when the defect concentrations exceed critical values.

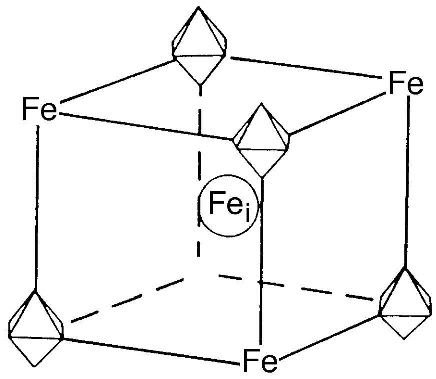


Figure 1-19. The basic unit for defect clusters in $Fe_{1-y}O$ comprising four vacancies (illustrated as boxes) and one interstitial ion.

The defect cluster in question might be denoted $(4v_{Fe}Fe_i)^{6/}$.

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

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+x}, the maximum value that x 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.

Extended defects, 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. This process may be illustrated 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 W_nO_{3n-1} and Ti_nO_{2n-1}. In this way the crystals may be able to have variable composition and may as such be termed nonstoichiometric.

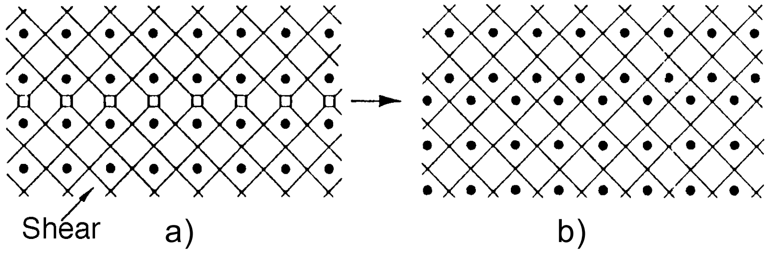


Figure 1-20. Schematic illustration of an extended defect and the formation of shear planes. The black circles represent the metal ions, the oxygen ions are located at the intersections of the mesh while the squares represent the oxygen vacancies. a) illustrates the alignment of oxygen vacancies and b) the elimination of oxygen vacancies and the formation of a shear plane.

The schematic depictions of defective lattices 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.

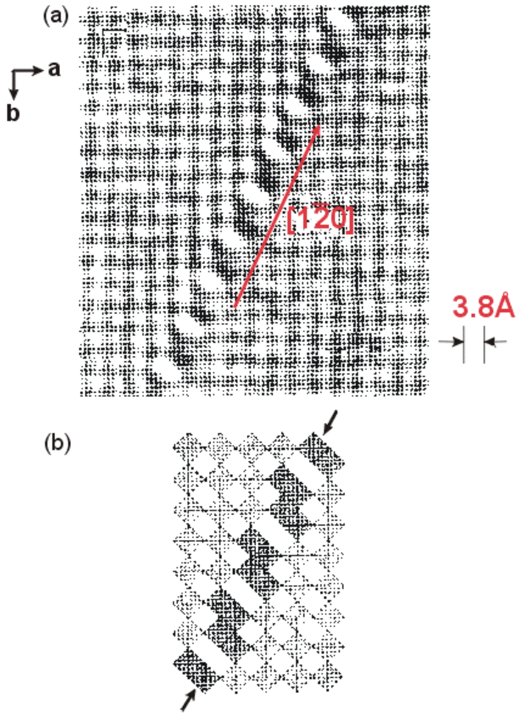


Figure 1-21. Real and simulated image of shear plane in WO_{3-x}. From Shriver and Atkins: Inorganic Chemistry.

Modulated structures/infinitely adaptive structures

Some oxide systems 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-Ta_2O_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. In competition with this minimisation of enthalpy with perfect, stoichiometric lattices, we have the tendency of increasing the entropy at $T > 0$ K and this is done 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. The overall defect structure is a result of energy minimisation by the enthalpy and entropy of formation and mixing, the electroneutrality condition (charge balance), mass balance, and preservation of the structure (site ratio balance). A defect is denoted 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 charge ($^\bullet$ or $^\prime$).

Further reading

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Exercises

1. Translate the defect names used in Fig. 1-1 and 1-2 into your first (or second) language.
2. Calculate the number of atoms in the unit cells of Figs. 1-7 and 1-8.
3. Calculate the number of atoms in the unit cells of Fig. 1-4 (a) and (b).
4. Calculate the number of ions of each kind in the cells in Fig. 1-9 and 1-13.
5. Calculate the number of atoms and voids in the cells in Fig. 1-6.

6. Calculate the volume filling ratio of balls in the structures of Figs. 1-4 (b), 1-4 (a), 1-7, and 1-8.
7. Why are metals intuitively 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 oxygen 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. Write the Kröger-Vink notation and the electroneutrality condition for the possible species and defects in a material of your choice – preferably a compound you are working with.
14. For the materials and list of defects in Exercises 10-13, write the electroneutrality condition.
15. Write the electroneutrality condition for defects in boron-doped silicon. Write the electronuetrality condition for defects in phosphorous-doped silicon. Write the electroneutrality condition for pure (undoped) silicon.
16. Suggest an electroneutrality condition for Y-doped ZrO_2.
17. Write an electroneutrality condition for MO_{1-x} (hint: includes an oxygen defect and electronic defects).
18. Write an electroneutrality condition for MO_{1+x}.
19. Write an electroneutrality condition for $M_{1-x}O$.
20. Write an electroneutrality condition for $M_{1+x}O$.