

Physical and Chemical Properties Related to Defect Structure of Oxides and Silicates Doped with Water and Carbon Dioxide*

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19.1 INTRODUCTION

The essential feature of crystals is anisotropy of their mechanical and also optical, magnetic, or electrical properties that is due to the regular ordering of the atoms, ions, or molecules forming the crystal lattice. However, the real crystals always deviate from the ideal crystalline structure and contain some structural defects (e.g., vacancies or dislocations) or foreign atoms replacing the proper atoms in the crystal and/or occupying interstitial positions. The number of defects also depends, among other factors, on the purity of the crystalline substance. In particular cases the presence of even small amounts of defects may strongly influence physical and chemical properties (electrical conductivity, thermal, spectral, and also catalytic properties) of solid oxides.

Although the defect state of transition metal oxides has been frequently investigated and is relatively well recognized, that of the alkaline-earth metal oxides became the object of serious studies only in recent years. Of special interest are the studies carried out by F. Freund and his collaborators (1980, 1982, 1985, 1991) in which the role of defects in the processes of incorporation of water and carbon dioxide molecules into the lattice of magnesium oxide has been elucidated. Similar processes may also occur in the other alkaline-earth metal oxides, CaO, SrO, and BaO, as well as in silica and silicates. They are also now gaining increasing importance for studies of the Earth's inner structure and some processes in tectonically active regions. The aim of the present paper is to review the physicochemical fundamentals of these processes. Our attention is focused at first on magnesium oxide as the model system, and subsequently it is shown that the results obtained are of general importance in the case of other oxides, silica, and silicate minerals.

19.2 GENERAL PROPERTIES OF MAGNESIUM AND OTHER METAL OXIDES

MgO belongs to the family of alkaline-earth metal oxides, like CaO, SrO, and BaO. They are ionic crystals exhibiting high melting temperatures.

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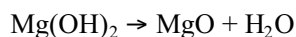
MgO is an ideal insulator (dielectric) at temperatures up to 200–230°C. At higher temperatures (250–400°C) it becomes a weak conductor. The surface charge of its crystals changes from negative to positive as the temperature rises.

At temperatures over 450°C, a large increase of conductivity is observed. A strong positive charge is observed on the crystal surface.

Magnesium oxide and the other alkaline-earth metal oxides form crystal lattices of the sodium chloride type presented in Fig. 19.1. In this lattice each cation is surrounded by six oxygen anions, the centres of which form the corners of an octahedron, as presented in Fig. 19.1 by six oxygen atoms. A similar octahedron is also formed by six cations around oxygen atoms.

19.2.1 Production of MgO of Very High Purity

Magnesium oxide is most frequently obtained by thermal decomposition of magnesium hydroxide or different magnesium salts at temperatures of 550–1000°C. For example,



Synthesis of magnesium oxide of highest purity is difficult. MgO may be easily contaminated by the traces of impurities present in the substrates from which it was

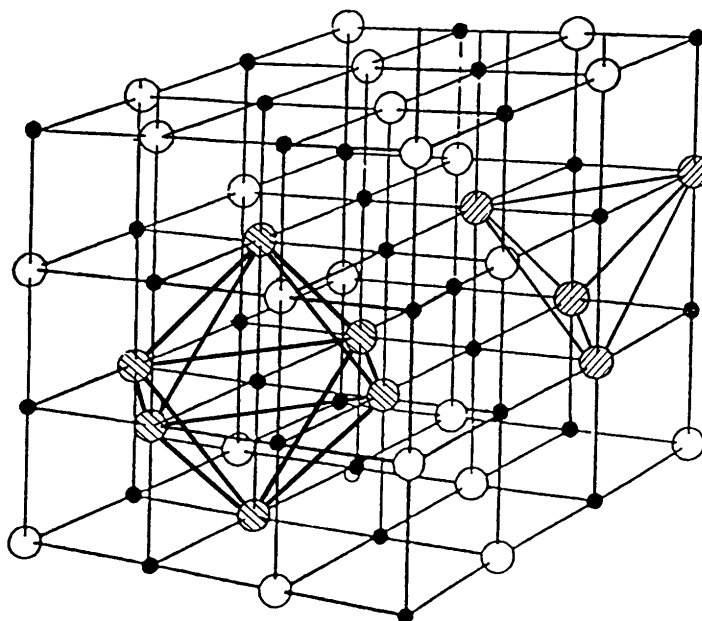


Figure 19.1 Crystallographic network of MgO or CaO; open circles, ions of oxygen; black circles, ions of magnesium or calcium (tetrahedron and octahedron are visualized).

obtained, but also by water and carbon dioxide molecules taken from the atmosphere. The removal of both latter impurities is done by fusing MgO (m.t. 2800°C) in an electric arc. This method is used nowadays to produce MgO of highest purity, even higher than 99.99% (weight). It is possible to obtain crystals a few centimeters long (0.1–7) and about 2 cm wide.

According to their purity, the crystals are denoted as follows:

4N: MgO of 99.99% purity

3N: MgO 99.9% purity

DN: MgO, commercial product

Table 19.1 shows the content of metal cations in MgO crystals of the various purities.

In recent years it has been also stated that magnesium oxide may contain minute amounts of elemental carbon. The formation of this impurity playing the role of lattice defect is discussed in Section 19.5.

Table 19.2 shows average contents of carbon in MgO of different purity.

Table 19.1. Contamination of Pure MgO Crystals.

Al	10–70	Fe	20–30
Ca	7–50	Ti	5–20
Si	5–15	Ni, V, Cr, Zr, Na, K, P	1–5

Note: Impurities given in wt-ppm; particles per million as referred to weight. Reprinted from Wengeler *et al.*, *J. Phys. Chem. Solids* **41**, 59–71. Copyright 1982, with permission from Elsevier Science.

19.2.2 Dissolution of H₂O in MgO Crystal

At proper conditions (temperature, water vapor pressure, *etc.*), magnesium oxide may incorporate some amount of water. This process occurring without a change of MgO crystalline structure will here be called dissolution.

The dissolution of water in magnesium oxide, which can be verified by chemical analysis, results in the formation of a number of lattice defects that are described in the following sections.

Table 19.2. Carbon Content in MgO of Different Purities.

Sample	wt-ppm	at-ppm
MgO 3N	~788	~2625
MgO 4N	~76	~253
MgO DN	~488	~1625

Note: Referred to weight and atom number. Reprinted from Wengeler and Freund, *Mat. Res. Bull.* **15**, 1241–1245. Copyright 1980, with permission from Elsevier Science.

It was found that the mechanism of dissolution of carbon dioxide and oxygen in MgO and CaO is the same and supplies analogous products.

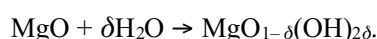
In the same way water is also dissolved in silicates, aluminosilicates, and thus also in rocks. It appears that in a major portion of rocks there exists “dissolved” water in an amount comparable to its total content in oceans, rivers, and air on a global scale. Studies on magnesium oxide should be treated like model studies, made on a very pure substance with strictly specified properties.

19.2.3 Mechanism of Incorporation of Water Molecules into Magnesium Oxide

Incorporation of a water molecule as a component of the crystal structure of solid oxide generates OH⁻ groups occupying anionic positions in the crystal lattice:



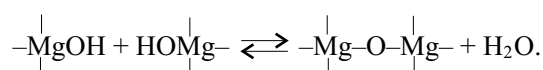
It is possible to describe the dissolution of H₂O in MgO also in the form of an equation:



This indicates that in magnesium oxide doped with water molecules, the number of occupied anionic sites in the crystal lattice is greater than that of cationic ones. The excess of anions has to be compensated by an equal number of cationic vacancies.

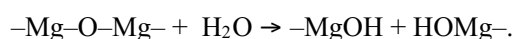
19.2.4 Defects in Crystal Lattice MgO.–

Formation of MgO from magnesium hydroxide can be presented as spatial polycondensation combined with water release:



At higher temperatures (e.g., 500°), the equilibrium of this reaction is moved to the right. Nevertheless, even at temperatures as high as 1000–3000°C, part of the hydroxyl groups still remain preserved.

In contrast, melted pure MgO at a very high temperature (e.g., in an electric arc, ~3000°C) absorbs or dissolves a certain amount of water:



It should be here observed that in both cases – magnesium oxide obtained from hydroxide and magnesium oxide fused at the presence of humidity – we deal with essentially the same type of product in which atomic ratio (O + OH)/Mg > 1. In both cases the same cationic and anionic point defects are present.

19.3 SYMBOLS AND CLASSIFICATION OF DEFECTS IN MAGNESIUM OXIDE

19.3.1 Symbols of Defects and Their Configuration in Crystal Lattice: The Kröger Notation

Description of defect states of solids, the formation of defects, and their equilibria has been greatly facilitated by the introduction of special symbols, the so-called Kröger-Vink symbols (Kröger, 1964).

The defects that are of importance to the problems discussed in this paper are called point defects: defects limited to only one site in crystal lattice, such as a missing atom from a cationic or anionic site that thus creates a vacancy, or an interstitial atom (an atom inserted between regularly occupied sites). Also included among point defects are foreign atoms situated on cationic, anionic, or interstitial positions.

Dots or primes indicate the relative electrical charge of the defects. The charge on the defect may be either higher or lower than that of the atom in the place of which the defect is situated. For example, a cationic vacancy V_{Mg}'' is equivalent to the lack of two elementary positive charges and must be considered as bearing two negative charges, which is marked by two primes, V_{Mg}'' . On the other hand, an O^- ion that has lost one electron becomes more positive than O^{2-} and is marked with one dot, O^\cdot .

19.3.1.1 Symbols of Vacancies

V_{Mg}'' means vacancy of Mg^{2+} (lack of magnesium ion).

Fe_{Mg}^x ion Fe^{2+} substitutes for Mg^{2+} .

(i) means interstitial position.

19.3.1.2 Symbols of Different Groups

OH^\cdot means OH^- substituted for O^{2-}

O^\cdot means O^- substituted for O^{2-}

$\begin{pmatrix} \text{O}^\cdot \\ \text{O} \end{pmatrix}$ means O_2^{2-} substituted for O^{2-}

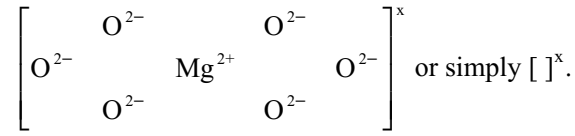
O^x means O^{2-} on O^{2-} lattice site

e means free electron

h^\cdot means lack of electron, electron hole

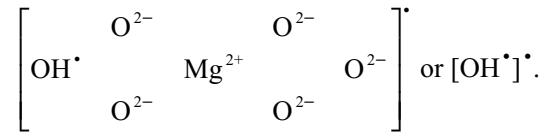
X_i' means ion in the interstitial position

Such processes as dissolution of water or carbon dioxide in magnesium oxide are usually connected with the formation of more than one type of point defect. In many cases they are assumed to be situated in the immediate vicinity of the cation and hence – as has been indicated by Freund – it is convenient to take into consideration a somewhat larger ensemble of atoms in the lattice, which enables us to represent more clearly the defect state of the oxide. For example, Freund takes into account the section of crystal lattice comprising one cation Mg^{2+} and six O^{2-} anions forming its immediate vicinity. Such a complex $[\text{MgO}_6]$ may be represented as

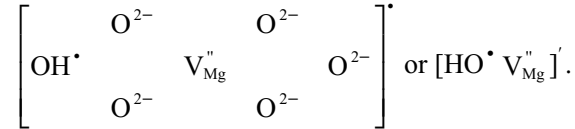


The symbol x means that the complex $[\text{MgO}_6]$ is electrically neutral with respect to the rest of the lattice.

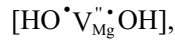
The substitution of O^{2-} (O^x) by OH^- (OH^\bullet) is symbolized by



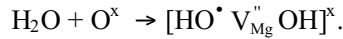
The substitution of O^{2-} by OH^- with simultaneous formation of cationic vacancy gives



Substitution of two O^{2-} by OH^- with simultaneous formation of cationic vacancy leads to the complex

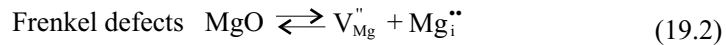


which may be formed, for example, by incorporation of water into magnesium oxide:

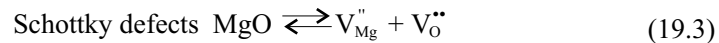


19.3.2 Defect Types

In the alkaline oxide, a solid with ionic character like MgO , the most typical defects are the Schottky and Frenkel ones. They represent intrinsic lattice defects:

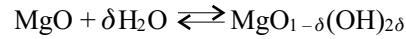


(a Mg^{2+} ion from a nodal position of the ideal crystal MgO is transferred into interstitial position $\text{Mg}_i^{\bullet\bullet}$, leaving at its site a cation vacancy V_{Mg}'').

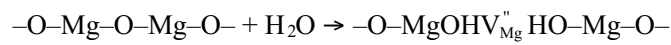


(a magnesium ion Mg²⁺ and oxygen anion O²⁻ both are transferred from the ideal lattice of MgO into interstitial positions leaving at their sites cation and anion vacancies).

During MgO crystallization in the presence of water, there originate – besides intrinsic defects – extrinsic defects as well. This can be described by the general equation



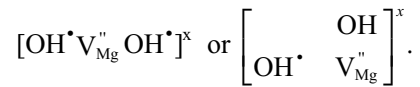
for a reaction that introduces δ water molecules into the crystal lattice of MgO. More detailed mechanism of this process is represented by the following scheme:



This shows that among the hydroxyl groups the cation vacancies V_{Mg} are created.

There exist different extrinsic defects, containing cation vacancies, depending on the number of OH groups introduced into MgO and on their space distribution around cation vacancy:

1. Defects with a fully compensated charge; they appear in the various space configurations of vacancies and OH⁻ groups:



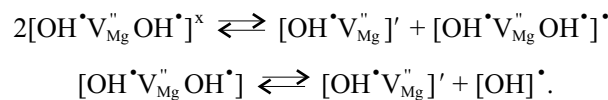
2. Defects with partially compensated charges:



3. Defects with over-compensated charges



All defects of these kinds can react with each other and regroup into other kinds of defects, depending on temperature and pressure conditions:

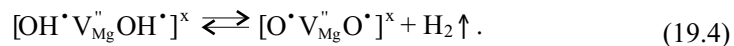


All these defects are important in reactivity, catalytic, electric, and magnetic properties of the oxides – magnesium oxide as well as the calcium, strontium, silicon, and aluminium oxides.

19.4 HYDROGEN AND PEROXY GROUP FORMATION

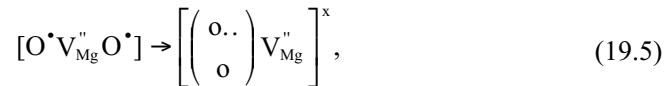
Especially interesting are systems where hydroxyl groups are situated close to each other, near the cation vacancy, e.g., $[\text{OH} \cdot \text{V}_{\text{Mg}}'' \text{OH} \cdot]^x$.

Between these hydroxyl groups a reaction connected with charge transfer takes place, leading to the formation of molecular hydrogen:



As Fig. 19.2 shows, amounts of gaseous hydrogen detectable by mass spectrometry are given off by magnesium oxide on heating above 400°C.

The two oxygen states can undergo a spin pairing process leading to a peroxy group,

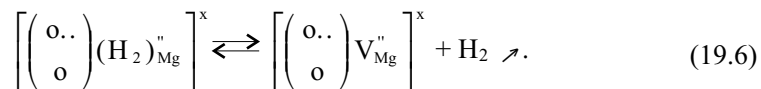


where

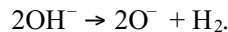


denotes the peroxy group O_2^{2-} with a spin pairing between O^- and O^- .

At room temperature, about 90% of the OH groups in MgO is transformed into molecular hydrogen H_2 and the peroxy ion. In the calcium oxide, this reaction takes place at a temperature of 700°C with about 50% efficiency:



The release of hydrogen takes place without participation of any external reducing agent. It has to be treated as a disproportionation process:



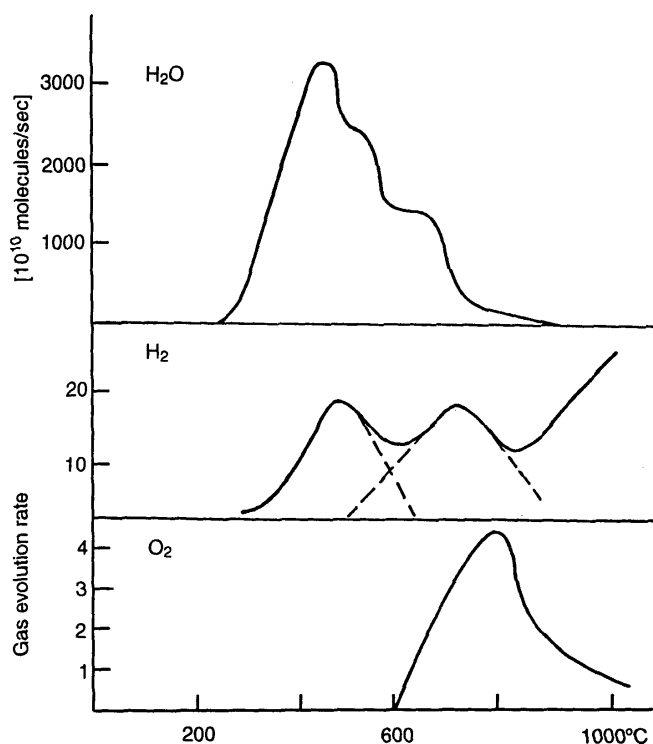


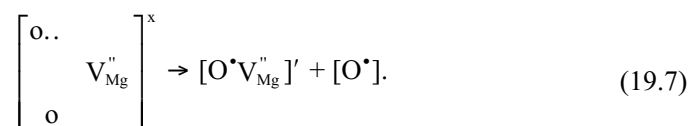
Figure 19.2 Water, hydrogen, and oxygen released during heating: $\text{Mg}(\text{OH})_2 \Rightarrow \text{MgO} + x\text{H}_2\text{O} + y\text{H}_2 + z\text{O}_2$ (compiled after Martens *et al.*, 1976).

19.4.1 Properties of the Peroxy Ion O_2^{2-}

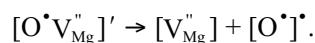
The peroxy ion is a point defect in which two O^- ions are connected by a strong 1.5 Å-long covalent bond, whereas the distance between O^{2-} ions in the MgO lattice is considerably longer, about 2.8–3.0 Å.

The molar volume of the peroxy group is small. An increase of pressure enhances the formation of the $\text{O}^- - \text{O}^-$ bond, but at the same time the core–core repulsion causes this bond to be rather weak.

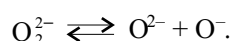
Peroxy ion O_2^{2-} is diamagnetic. Its position in the MgO matrix is close to a cation vacancy. At a temperature of 500°C this system disintegrates into two paramagnetic particles, $[\text{O}^\bullet]^\bullet$ and $[\text{O}^\bullet \text{V}_{\text{Mg}}'']^\bullet$:



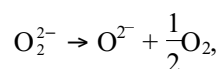
$[O^{\bullet}]^{\bullet}$ denotes the electron positive hole ("h") in the O^{2-} lattice. The group $[O^{\bullet}V_{Mg}^{\bullet}]$, which is the positive hole localized on a cation vacancy, disintegrates into a cation vacancy and another positive hole:



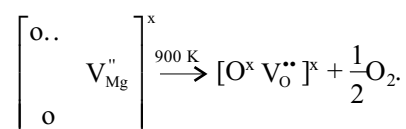
O_2^{2-} ions have coupled spins and are stable at lower temperatures. At 200–300°C their spin decoupling begins and formation of O^{\bullet} occurs:



At temperatures over ~700°C the peroxy ion disproportionates into molecular oxygen and an anion O^{2-} ,



or



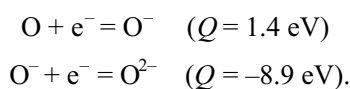
On heating MgO containing some dissolved water – the release of hydrogen is followed by the release of oxygen.

Figure 19.2 presents relationship of the heating temperature to volume of released oxygen and hydrogen.

19.4.2 Properties of the O^{2-} Ion

Despite what was believed earlier, when O^{2-} ions were considered one of the most stable form of oxygen, it is now well known that these ions are not stable in the gas phase.

Comparing the properties of O^{2-} and O^{\bullet} ions with respect to their electron affinities, we find that the affinity of oxygen atom is positive, 1.4 eV, while the affinity of the ion O^{\bullet} is negative, –8.9 eV (Vendenege, 1966; Edién, 1960):



This means that the O^{2-} ion situated in vacuum without influence of environment, should decompose itself into $O^{\bullet} + e^{-}$, releasing 8.9 eV (Vendenege, 1966; Edién, 1960). The O^{2-} ion was treated as very stable, because its properties were observed in-

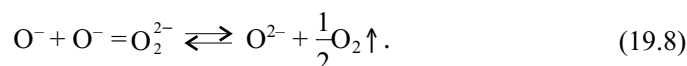
side a crystal lattice, e.g., MgO, where the O²⁻ ions are stabilized by Coulomb interaction: O²⁻– M_{Metal}²⁺ (Kathrein and Freund, 1983; Kathrein *et al.*, 1984).

19.4.3 Properties of the O⁻ Ion

From the point of view of a chemist, O⁻ is a free radical. Its outer shell is unfilled.

From the point of view of a physicist, O⁻ represents a delocalized state of electron in the oxygen lattice. At very low temperatures spin O⁻ can be localized on any oxygen ion, but with increasing temperature the O⁻ ion becomes fairly mobile. It has a negative charge smaller than the surrounding O²⁻ matrix, and hence it is named a “positive hole”.

Being very mobile, the positive holes diffuse easily to the crystal surface, where these defects combine, producing a peroxy ion O₂²⁻. At temperatures > 800 K the latter disintegrates into lattice oxygen, molecule oxygen, and an anion vacancy. Emission of oxygen begins above 600°C (Fig. 19.2) and reaches its maximum at about 800°C (Kröger, 1964):



19.5 ATOMIC CARBON IN MgO CRYSTALS

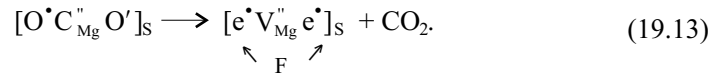
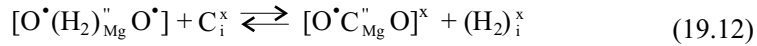
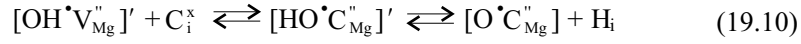
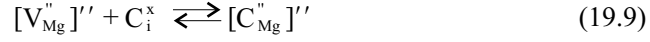
In the early 1980s the discovery of atomic carbon inside MgO crystals of very high purity was a real surprise, as analyses made according to classical methods showed the absence of ions such as CO₃⁻, CN⁻, COOH, and organic compounds (Freund *et al.*, 1980a, 1980b, though the possible presence of atomic carbon was not investigated).

One could think at that time that contamination of MgO with carbon is due to the use of graphite electrodes during melting and crystallization of MgO in an electric arc. It turned out, however, that the atomic carbon was always present in the MgO crystal, regardless of its method of preparation. Now we know that atomic carbon in the MgO crystal originates from CO₂ contained in the air. Most often it gets in by chemisorption on the surface, but it also escapes from the MgO lattice (partially) in the form of CO₂ and CO, taking away oxygen from the lattice.

The distribution of atomic carbon in the MgO lattice is very irregular. Its concentration (Wengeler *et al.*, 1980a) inside the lattice and on the surface varies with temperature and differs in a thin superficial layer from that inside the crystal lattice. Carbon dissolved in MgO is very mobile. At high temperatures (Wengeler *et al.*, 1982), 300–450°C, it is more regularly distributed; as temperature decreases, the carbon atoms migrate to the surface and their concentration in the layer next to the surface becomes many times higher than that inside the lattice. An exceptionally high concentration has been stated around room temperature (Henderson and Wertz, 1977).

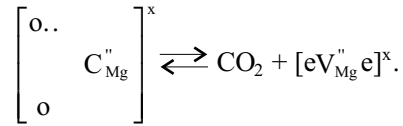
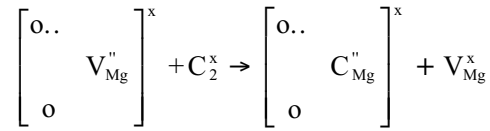
As mentioned, atomic carbon in MgO takes an interstitial position in form C_i^x , which enables its high mobility.

Hereafter we present reactions between MgO lattice defects and atoms of carbon occupying an interstitial position (Freund and Wengeler, 1982):



Here, subscript S means surface and $[e \cdot V_{Mg}^{''} e \cdot]$ corresponds to the so-called centrum F (a strong electron donor) (Knobel and Freund, 1980).

As an example, we present the reaction between carbon in an interstitial position and a peroxide ion near a cation vacancy:

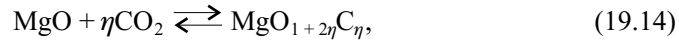


In this reaction carbon takes place of the cation vacancy (Kathrein and Freund, 1983); carbon plus peroxide ion decomposes to carbon dioxide and center F (centrum F). Centrum F is a source of electrons “consumed” in different transformations of intrinsic and extrinsic lattice defects.

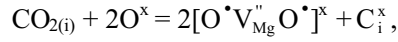
19.6 DISSOLUTION OF CO₂ IN MgO

Similar to the case of H₂O, dissolution of CO₂ produces many defects in the MgO lattice (Freund, 1980). In most cases, they are cation and anion vacancies and different active forms of oxygen. MgO crystal heated up to ~700°C emits CO₂ and, in most cases, also CO.

The dissolution of CO₂ in MgO can be described by the equation

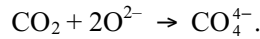


or otherwise

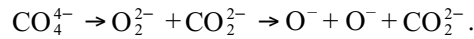


where C_η means the incorporation of η parts of CO_2 into the MgO structure and the formation of η carbon atoms. One interstitial atom of carbon, two cation vacancies V_{Mg}'' , and four positive holes (O^\bullet) are produced from one particle of CO_2 dissolved in MgO.

An interstitial carbon atom is situated in the MgO crystal lattice between four oxygen ions that form around it the corners of a tetrahedron, as shown in Fig. 19.1. Such $[\text{CO}_4]$ complex may be treated as a CO_4^{4-} ion:

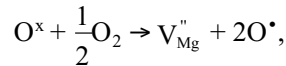


This ion disintegrates to peroxide ion, which is a source of positive holes and CO_2^{2-} ions:



19.7 DISSOLUTION OF O₂ IN MgO

Gaseous oxygen under the influence of high pressure dissolves in the MgO lattice, forming a cation vacancy,



or



19.7.1 Infrared Spectra of MgO Crystals

It has long been well known that MgO samples obtained by different methods contain OH groups. In the years 1960–1980 this fact aroused particular interest, because the infrared spectra of the highest purity MgO samples considerably differ from the theoretically calculated spectra. By applying the conditions of symmetry for different surroundings of the OH group, a “synthetic” IR spectrum of OH groups in MgO was simulated.

The upper part of Fig. 19.3 presents the IR spectrum of stretching oscillations, theoretically calculated for OH groups in MgO. It shows “discrete” bands for IR signals of defects (Freund and Wengeler, 1982). I: $[\text{OHV}_{\text{Mg}}^{\text{II}}\text{OH}]^{\times}$ and II: $[\text{OHV}_{\text{Mg}}^{\text{I}}]^{\cdot}$, and a diffuse band for H_i . The band is blurred, because a proton in the interstitial position is partially delocalized.

The lower part presents the real IR spectrum of 4N MgO crystal of 99.99% purity.

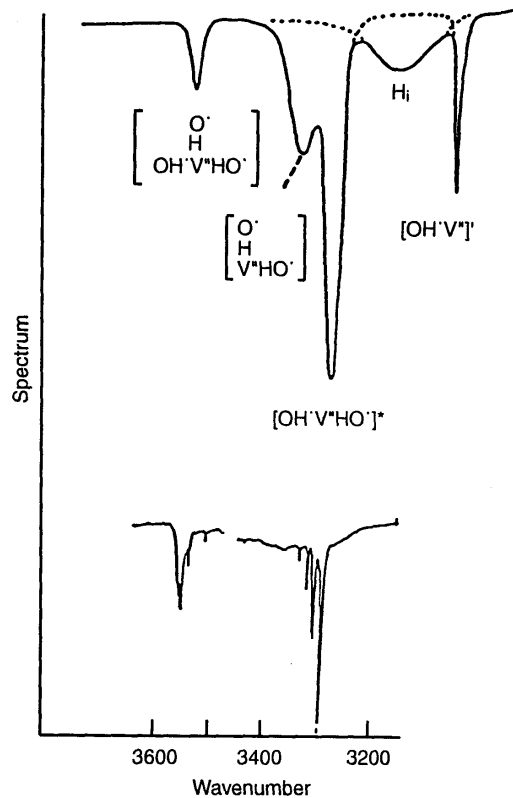


Figure 19.3 The IR spectrum of MgO: upper curve, the synthetic spectrum related to the different types of OH groups at cation vacancies (compiled after Freund and Wengeler, 1982a); lower curve, the observed infrared spectrum with disturbances of the OH oscillator for the partly compensated vacancy $[\text{HO}^{\cdot}\text{V}_{\text{Mg}}^{\text{II}}]$ in the presence of interstitial carbon C_i^{\times} (compiled after Wengeler and Freund, 1980b).

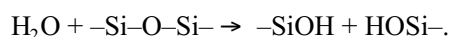
Comparing the synthetic spectrum with the spectrum of this pure MgO crystal, one can see some differences. The general design of the band pattern is preserved. In the spectrum of the original crystals, some bands are markedly diffused and partially displaced.

However, the main differences in IR spectra are due to the presence of carbon atoms in the crystal lattice. A carbon atom can occupy different positions in the crystal lattice: the position of a cation vacancy $\text{C}_{\text{Mg}}^{\times}$ or an interstitial position C_i .

19.8 MECHANISM OF WATER DISSOLUTION IN MINERALS

In the preceding sections the mechanism of dissolution of water molecules in magnesium oxide has been described. The experiments most important for this problem were carried out using crystals of very high purity as the model system. However, the same phenomena of water dissolution were observed not only in magnesium and calcium oxides, but also in silicon oxide and aluminum and iron oxides.

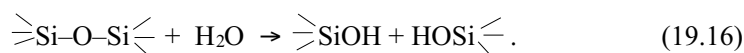
In all these cases the introduction of water molecules into the crystal lattice causes formation of hydroxyl groups. Hydroxyl groups can transform into the peroxide ions O₂²⁻, and these, in turn, into positive holes. The same observations relate to silicate minerals. In this reaction one proton from the H₂O molecule is transferred onto O²⁻ in the lattice of the solid oxide. In polymeric oxides (e.g., glasses), water hydrolyzes the Si–O–Si group, producing silanol groups:



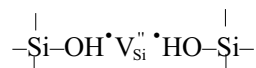
The world of rocks is only apparently dry; in reality, all rocks comprise in their structures a great amount of water. As in the case of magnesium oxide, silicates during their formation or crystallization absorbed certain quantities of water, which was incorporated into the structure of silicate minerals. This water did not evaporate at temperatures of the order of 1000°C.

A similar situation occurs when minerals are subjected to high temperature and pressure in the presence of water. The mechanism of water dissolution is analogous to the previously described phenomenon of water dissolution in MgO.

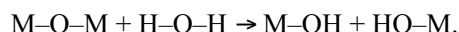
The dissolution of water in oxides can be described as the transfer of a proton from H₂O onto the ion O²⁻ in the crystal lattice; in silica it produces two hydroxyl groups:



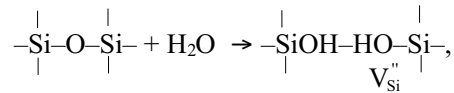
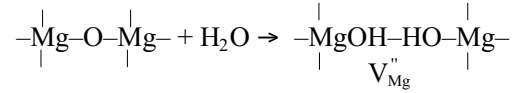
When such a system is formed inside a crystal, a cation vacancy appears. Its charge compensates the charges of two hydroxyl groups (Stone and Walrafen, 1982; Freund, 1994; Freund *et al.*, 1994):



The basic reaction between metal oxides and water molecules is the breaking of bonds between metal and oxygen,



Comparing reactions of water molecules with magnesium oxide and silica, aluminum, or iron oxide,



one should take into account that magnesium oxide incorporates molecules of water much more easily than does silica. This means that the Mg → O bond is more strongly polarized than the Si → O bond. In both cases two hydroxyl groups are formed from water.

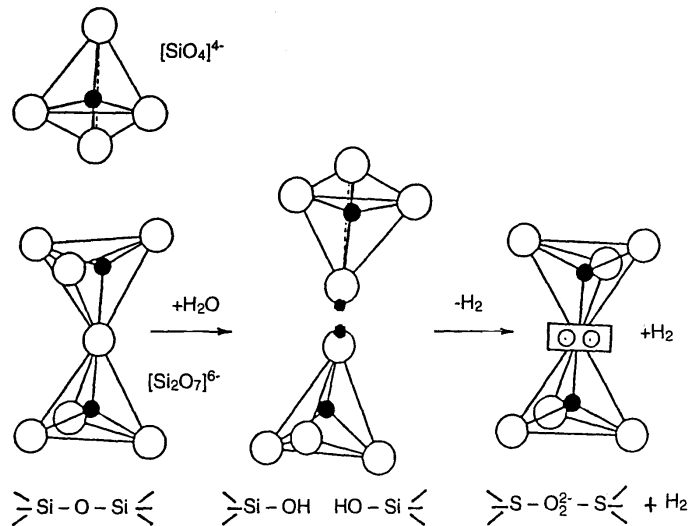
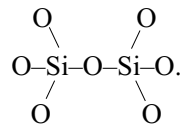


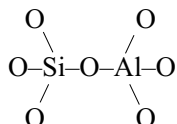
Figure 19.4 Schematic structure of silicate and its dimers; emission of H_2O and H_2 , and formation of its peroxide ions.

In the case of silicates the basic unit in crystal structure is the tetrahedral group $[\text{SiO}_4]$. Its structure is presented in Fig. 19.4 (Wengeler and Freund, 1980b).

Combinations of these tetrahedrons produce a great number of possible structures. The simplest system is the bonding of two tetrahedrons by common corners (Fig. 19.4):



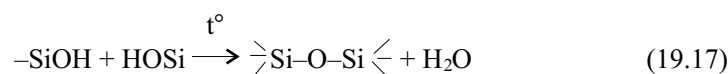
In the case of aluminosilicates we will get



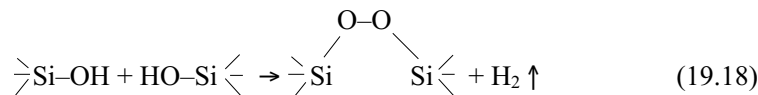
19.9 FORMATION OF PEROXY IONS AND POSITIVE HOLES IN SILICATES

The introduction of water molecules into various systems composed of a continuous crystal lattice $n(\text{SiO}_2)$, such as quartz, or of more loosely bonded tetrahedrons $[\text{SiO}_4]$ causes hydrolysis of the Si–O–Si bond and formation of OH groups. The spatial distribution of the OH groups plays a basic role in some reactions. Practically, the two OH groups can undergo the following two reactions:

1. Release of water molecules, i.e., inverse reaction to hydrolysis:



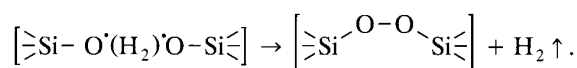
2. Release of hydrogen:



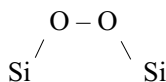
These reactions depend on the spatial distribution of the OH groups (and on temperature and pressure conditions). If the OH groups are situated sufficiently close to each other (the situation when OH groups are formed by hydrolysis of the $\text{OH}-\text{Si}-\text{O}-\text{Si}$ group), the release of molecular hydrogen is possible. The mechanism of these reactions includes charge transfer:



At higher temperatures gaseous hydrogen is released, and at the same time the spins of two oxygen O⁻ ions become coupled (paired):



The formation of the peroxide group connected with two O–Si groups occurs parallel with the formation of a H₂ molecule. Here, the group



has a peroxy character and easily undergoes a disintegration.

The presence of hydrogen bonded in the form of hydroxyl groups in silica was confirmed by studies of silicates, rocks, quartz *etc.*, using infrared analysis. Very good examples here are the studies on hydroxyl groups and molecular hydrogen in olivine (MgFe)SiO₄ and silicate glass.

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