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# Interfacial Separation of Particles

S. Lu, R.J. Pugh, E. Forssberg

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## **Interfacial Separation of Particles**

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# Interfacial Separation of Particles

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## Preface

There are various interfacial separation techniques, developed so far, such as froth flotation, foam separation, coagulation and flocculation, membrane separation, etc. Interfacial separation has been finding wide application in many industrial fields, such as mineral processing, environmental protection, hydrometallurgy, bioengineering, food and beverage industry, chemical industry and others. Many books are available dealing separately with the individual interfacial technique, for example, in the area of froth flotation, flocculation, filtration, etc. However, up-to-date no extensive literature has been published which includes the general theoretical fundamentals of all these interfacial separation techniques.

From the phenomenological viewpoint, all these techniques indeed are distinct from each other, and it seems no common characteristic features exist among them. But, more deep investigation reveals that all these techniques have a common scientific basis, based on differences in the surface and interface properties of particles. and all types of the technological process are carried out at specifically developed interface of two or three different fluid phases. The most important task for interfacial separation technology is to enhance and create as large as possible distinctions in interfacial properties of particles to be separated, and to provide sufficient area of two- or three-phase interface, mostly gas/liquid or liquid/liquid phase. Therefore, it is reasonable to suggest a general name - *interfacial separation of particles* to characterize all these techniques. Interfacial separation is particularly important and in most cases is the key technology for controlling performance of fine and ultrafine particle processing because the interface properties are dominant factors.

At present, more and more new techniques of interfacial separation have been developed and applied in various practical fields. Hence, in this book, the authors attempt to discuss the general scientific bases of various interfacial separation techniques, developed so far, and to provide an overview of the typical techniques, especially their recent growth in developments in the fields of interfacial separation. Chapter 1 is a general description of interfacial separation, its definition and coverage. Chapters 2-4 discuss the scientific bases of interfacial separation. More attentions have been paid on the surface and interfacial properties of fine particles in aqueous solutions, the interactions between solid particle and the surrounding medium, and, particularly, between solid particles in the suspensions. Chapter 5 describes the physical, physicochemical and other characters of particle suspensions, because interfacial separation is always undertaken in a solid particle suspension, the characteristic features of the industrial suspensions are important. Chapters 6-11 describe separately the typical interfacial separation processes, available so far. In these Chapters, the theoretical principles, technological characters, recent growth in techniques and their practical applications are provided.

In this book, an emphasis has been made on the particle dispersion in suspensions, since dispersion control is crucial for a successful interfacial separation. Chapter 10 has been specifically devoted to deal with the dispersion of particles in suspensions. The last Chapter, Chapter 12, compiles and describes the most important equipment, related to interfacial separation. Chapters 1 - 5, 8 - 11 were written by S. Lu, Chapter 6 was written by R. Pugh and S. Lu, Chapter 7 was written by R. J. Pugh, and Chapter 12 was written by E. Forssberg. All the manuscripts of this book have been discussed several times, revised and up-dated by all the authors together.

This book was prepared by the authors, as an aid to long term teaching programs and research works. The book is intended to provide the theoretical understandings and the more promising developments of the interfacial separation technology and to reflect as wide as possible, the world-wide achievements in this field. With this aim, we quoted materials not only from the English literature, but also from the Chinese, Russian and Japanese sources. We hope this book will be able to assist the readers in acquiring the scientific basics of interfacial separation technology and more broad background of industrial suspensions. In addition, it is aimed to assist teachers, and industrial researchers to gain information concerning principles, developments and applications of interfacial separation of particles in different areas. This book also may serve as a useful text for the post-graduate students in universities. Since interfacial separation is an interdisciplinary field, it may prove to be a useful reference in many related industrial and other economic fields.

Finally, it is a pleasure to acknowledge those whose contributions helped bring this book into existence. Those people are too numerous to mention individually, but we wish to thank in particular Professor Wei Tian, Dr. Qi Liu, Dr. Weixing Wang, Mr. Guangqing Han, Ms. Siv Bernhan, Dr. Yanmin Wang, Mr. Huiting Shen, Mr. Jirang Cui, Dr. Changsheng Peng and Dr. Hong Meng for their great helps.

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## CHAPTER 1

# 1. INTRODUCTION

## 1.1. CLASSIFICATIONS OF SEPARATION TECHNOLOGY

Separation technology has been widely used in many industrial fields and also in our daily life. According to the subject to be separated, separation can be classified into separation of homogeneous mixtures and separation of heterogeneous systems. Mass transfer separation of homogeneous mixtures in the liquid phases is a typical unit operation in chemical engineering. Whereas, the separation processes of the heterogeneous systems, involving the solid particles suspended in the liquid phases, perhaps are even more commonly encountered everywhere in the industrial practice, our daily life as well as in nature. Separation methods can be also categorized according to the separation work principles. Haruhiko (1998) suggested to classify the separation techniques into three groups: (i) phase equilibrium separation process, based on the equilibrium relationship between two phases; (ii) velocity difference separation process, or otherwise, field separation, in such a process a specific gradient field is created to induce the velocity difference of separated substances; (iii) reaction separation process, where the chemical or biochemical reactions are used to undertake the separation. In principle, these three groups of separation can be used to either homogeneous or heterogeneous systems. Nevertheless, the velocity difference separation process is more typical for heterogeneous systems.

Fig. 1.1 illustrates various separation processes including both the homogeneous and heterogeneous separation techniques and the corresponding applicable particle size ranges.

In the heterogeneous systems the separation methods for solid particles suspension are most varied. In principle, they can be further classified into two major groups of unit operations: the solid/liquid separation and the solid/solid separation between different types of solid particles. Thickening is a unit operation of solid/liquid separation based on the sedimentation of solid particles in liquid, whereas filtration is also a solid/liquid separation process with helps of pressure gradient field through filtration mediums. Heterogeneous particles, suspended in liquid phase, may be separated into individual groups of the constituent homogeneous particles in terms of the differences in the physical or physico-chemical properties of the particles, such as particle size, density, magnetic or electrical properties, surface wettability or even the solubility of

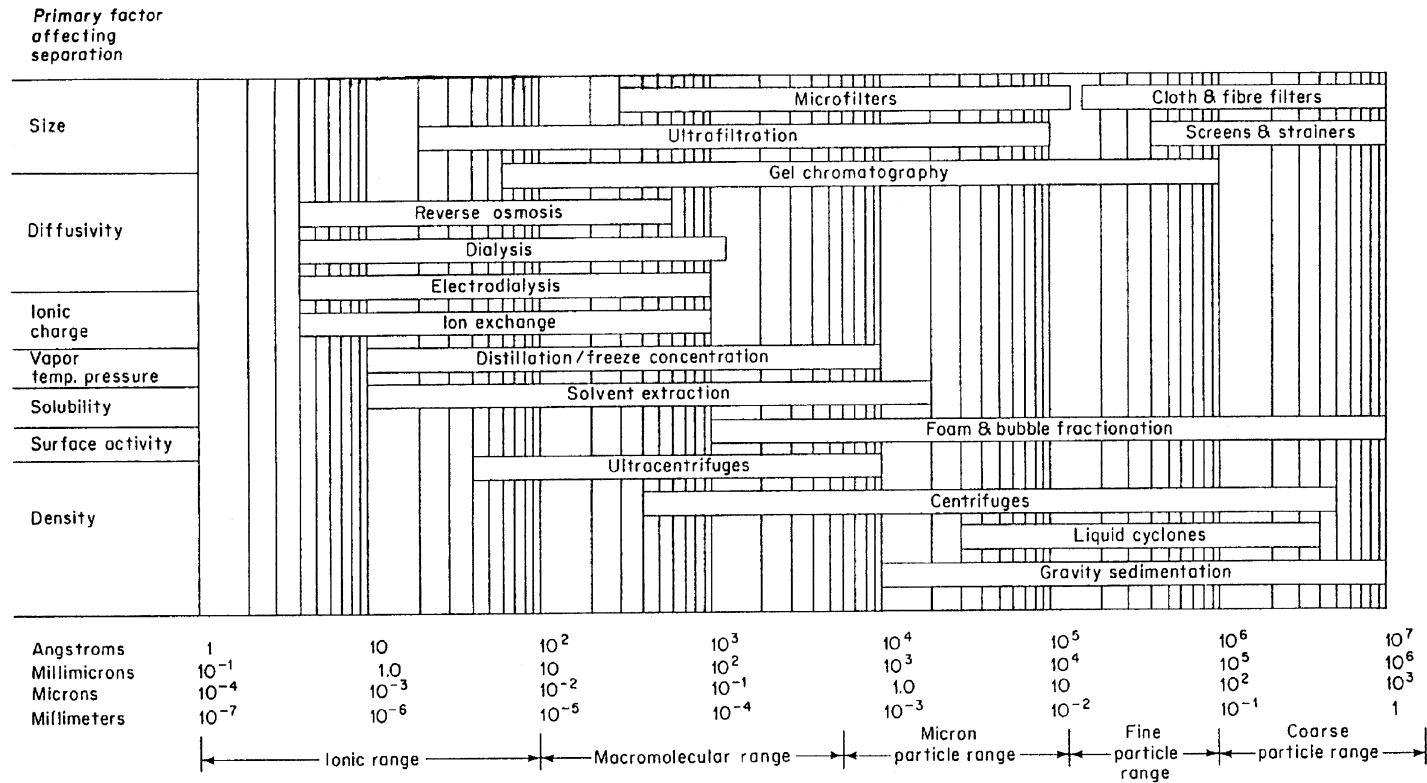


Fig. 1.1. Useful ranges of various separation processes (Schmeitzer, 1979, p.2-7)

particles, etc. For example, classification is a separation process based on the geometrical character of particles - particle size distinction. Magnetic separation is a separation method based on the difference in the specific magnetic susceptibility of particles. For a practical purpose, the separation techniques can be also classified into the following groups on the basis of work principles of the separation process: (i) physical methods; (ii) interfacial methods; (iii) chemical methods and (iv) bio-technical methods.

## **1.2. INTERFACIAL SEPARATION – A SPECIFIC CATEGORY OF SEPARATION TECHNOLOGY**

Interfacial separation is a specific group of separation technology in between the physical separation methods and the chemical separation methods. The work principles of interfacial separation are based on the distinctions in interfacial properties of substances to be separated. Laskowski (1982) analyzed separation methods in the field of mineral processing and suggested a special group of physicochemical separation methods. Later on, “Interfacial Separation” has been proposed (Lu, 1987; Lu and Wong, 1992) to describe all the separation processes based on the distinctions in interfacial property of substances to separate and through proper interface and colloid chemistry controlling.

As a matter of fact, interfacial separation perhaps is one of the most important separation technology, which has been comprehensively studied and widely applied in practice. Due to the high efficiency and selectivity of the process, interfacial separation has been expanding its application in processing and separation of fine solid or liquid particles as well as soluble substances over a variety of industrial fields.

A traditional and typical example of interfacial separation is froth flotation. Froth flotation has been developed for more than one hundred years and becomes the predominant separation method for sulphide minerals concentration. Froth flotation is also comprehensively applied to separation of metallic oxide, salt-type mineral, non-metallic mineral and other solid particle.

Despite its wide application, the effectiveness of conventional froth flotation is limited within a relatively narrow size range of particles be treated. Normally, the upper particle size limit of froth flotation is about 0.1 ~ 0.3 mm, while the lower size limit is approximately 5 ~ 10  $\mu\text{m}$ . Beyond the optimum size range, froth flotation can not work efficiently.

For the heterogeneous particles coarser than 0.1 ~ 0.3 mm, the physical separation methods have been proved effective and already applied commercially for a long time. However, the history of table flotation, an interfacial separation technique for coarse particles, can be traced back to the end of the 18 century. As an alternative to skin flotation, table flotation has



found its commercial application for separation of coarser sulfide particles up to 1 ~ 2 mm. It has been reported that the foam separation has also achieved satisfactory results for coarse particle separation. The upper size limit of foam separation reaches from 0.5 mm to 3 ~ 5 mm depending upon the density of particles.

On the other hand, processing and separation of particles with size below 10 ~ 20  $\mu\text{m}$  suspended in liquid phases are a commonly encountered task in the industrial practice and in our daily life. For example, the particle size of clay particles and bacteria cells ranges between several microns and even submicrons. Due to the significantly larger specific surface area of the fine and ultrafine particles, the interparticle interactions become significant and even dominant and the particle/liquid interactions are also changed. All these interactions may result in marked changes of aggregation/dispersion state of particles and specific hydrodynamic behaviors of particles in fluid, and even marked changes of chemical behaviors of particles in suspension are observed. All these factors seriously affect the separation process, make the process very difficult. But on the other hand, it suggests a possible way to solve such a problem – to utilize the interfacial phenomena in the system as far as possible for the fine particles separation.

The technological basis of interfacial separation is to utilize the distinction of the interfacial properties between the particles to be separated and to undertake the separation process at the specifically developed interface of two or three different fluid phases. Therefore, for interfacial separation, interactions between the solid/solid phases and between the solid/liquid phases, for three-phase systems, between the solid/gas and liquid/gas phases, are critical factors, which determine the success of the process. Thus the most important task for interfacial separation technology is to enhance and create as large as possible distinctions in interfacial properties of particles to be separated, and to provide sufficient area of two- or three-phase interface, mostly gas/liquid or liquid/liquid phase, for realization of the separation process. For fine particle separation, as an example, three principles are essential: (i) utilizing the distinction of surface properties between the heterogeneous particles to be separated, e.g. surface wettability, adsorption ability, surface electrical properties and the properties of adsorbed layer on particles etc.; (ii) size enlarging of the particles to be treated by means of selective aggregation of fine particles; (iii) providing as much as possible air/liquid or liquid/liquid interface for transporting the goal particles out from liquid phase, and sometimes, changing of the transport mediums, e.g. substituting air bubble by oil drop, improving its dispersion and so on.

### 1.3. CONTENT AND CLASSIFICATION OF INTERFACIAL SEPARATION

Generally, interfacial separation process consists of following unit operations:

- modification of particle surface properties, such as wettability, surface electrical properties, adsorption ability, etc., by means of chemical or physical treatment;
- adjustment of the aggregation/dispersion state of particles in suspensions by regulating the particle-particle interaction;
- selective attachment of particles at the specifically produced two phase interfaces, e.g. gas/liquid, oil/water interfaces under appropriate physical and hydrodynamic circumstances.

A variety of interfacial separation techniques for fine and ultrafine particles have been developed in laboratory as well as in pilot or full industrial scale. Also interfacial separation has attracted more and more attention in other economic fields.

Fig. 1.2 provides a classification of the interfacial separation techniques commercially used or developed in laboratories. The last columns denote the separating measures the technique uses.

It can be seen that interfacial separation technology can be used not only for heterogeneous systems, but also for homogeneous mixture systems to separate particles in the size range from several mm to as fine as molecular or ionic dimension. For separation of coarse particles, foam separation, skin separation, table flotation and others are used. Conventional froth flotation is effective and suitable to separate fine particles within the size range 0.1~0.01 mm. For the particles finer than 10~20  $\mu\text{m}$ , a variety of fine particle separation techniques have been developed. Membrane separation process and ion-exchange resin adsorption technique are the typical examples of interfacial separation for homogeneous system. Some techniques listed in the figure are quite old, some are novel. In recent years interfacial separation techniques have extended their usage to processing the colloidal particles and bacteria. For example, techniques of electrophoretic separation, colloidal and ion flotation, etc are rapidly exploited and developed. Ion flotation is a technique for separation of ions, however, according to its nature ion flotation is a heterogeneous separation rather than a homogeneous one, because the ions subject to be separated out forms colloidal precipitates with added agents prior to their flotation. There appeared some newly developed techniques for separation of molecules or ions utilizing interfacial properties and interactions of systems. The electrodialysis widely applied to the water purification is relied on the electrical properties of ions and the interaction of interfaces between ions

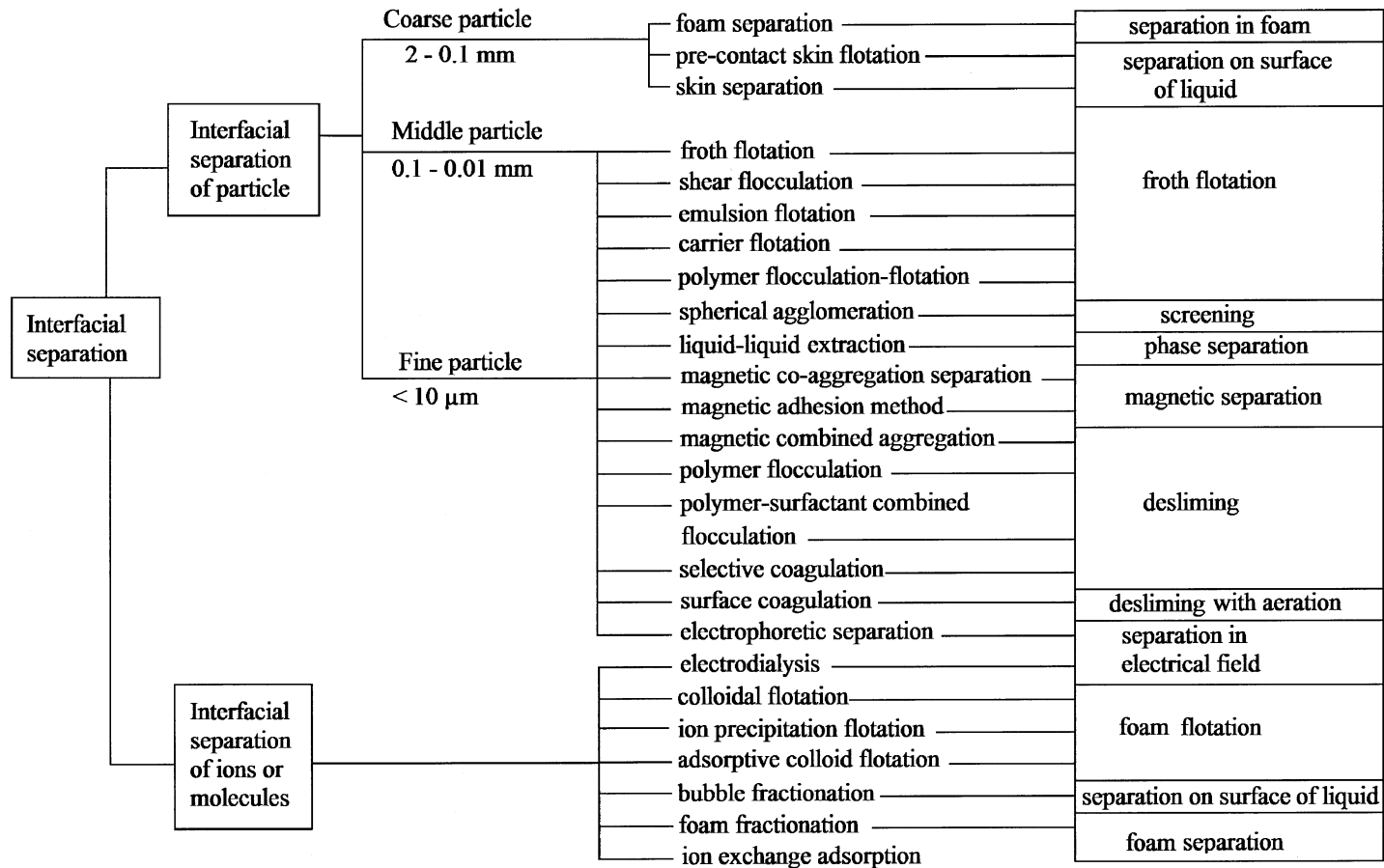


Fig. 1.2 Classification of interfacial separation techniques

and ion-exchange membrane and it is realized by means of selective permeation of ions under dc electrical field. It has been already proved that interfacial separation is an efficient method to process fine and ultrafine disseminated mineral particles and organic or inorganic fine particles of secondary resources. Interfacial separation has been also effectively applied in the field of water treatment, ultrafine material engineering, chemical engineering, biological engineering and others industrial and agricultural areas.

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## CHAPTER 2

## 2. SURFACE PROPERTIES OF PARTICLES

### 2.1. SURFACE OF SOLID PARTICLES

#### *2.1.1. THE STRUCTURE OF FRESH SURFACE OF PARTICLES AND THE DEGREE OF SURFACE UNCOMPENSATION*

In comminution of crystals, cracks occur in the crystal lattices and develop into cleavage planes along the direction of the weakest bonding force. Generally, the cleavage occurs between the two parallel lattice planes, where their lattice point density is greatest, where positive and negative ions are neutralized, where the chemical bonding force among the lattice points in the plate is the strongest, or the two lattice planes have the same charges. As far as actual mineral crystals are concerned, the nature of a cleavage plane can be determined only after many factors are taken into account. For example, in the lattice of sphalerite ( $\text{ZnS}$ ), the lattice interplanar distance is longest ( $2.36\text{\AA}$ ) along the (111) plane, but the breaks of sphalerite, in fact, occur along the (110) plane. The reason can be explained by the fact that the  $\text{Zn}^{2+}$  lattice plate and the  $\text{S}^{2-}$  lattice plate alternate with each other along the (111) plane and cause a relatively stronger bonding between the planes due to electrostatic attraction. Although the interplanar distance between (110) planes is shorter, every (110) plane of sphalerite lattice contains not only positive but also negative ions. This lattice plane appears to be electrically neutral thus the bonding force is strong inside the plane, while the interplanar bonding force is relatively weak. Therefore the cleavage usually occurs in the direction of (110) plane, as illustrated in Fig. 2.1. (Pan and Shao, 1979).

On the contrary, crystals such as quartz possess no comparatively weak bonding direction, i.e. their bonding forces are homogenous. This kind of the crystals consequently form irregular broken planes called “fractures”.

Layer silicates expose similar (0001) cleavage planes, but the broken bonds on the cleavage planes are different. Fig. 2.2 shows the structure of two groups of layer silicates: pyrophyllite ( $\text{Al}_2(\text{Si}_4\text{O}_{10})(\text{OH})_2$ ), talc ( $\text{Mg}_6\text{Si}_8\text{O}_{20}(\text{OH})_4$ ) group and muscovite ( $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ ), smectite group. In pyrophyllite and talc, the crystal layers are neutral, no electrical charge exposed on the basal plane, only weak van der Waals forces operate between the layers, thus the basal planes of talc and pyrophyllite are weakly unsaturated, thus hydrophobic. The advancing contact angle on the relatively randomly oriented talc mineral is

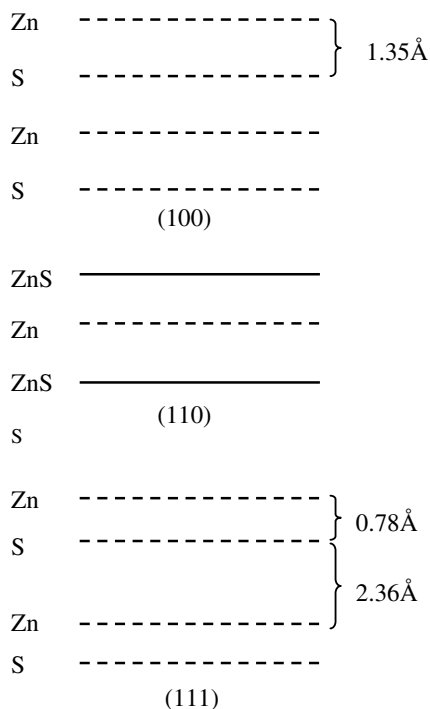


Fig. 2.1. Cleavage directions of sphalerite

about  $61^\circ$  and on the crystals on tape backing that have a preponderance of cleavage plane orientation, the advancing contact angle is about  $83^\circ$  (Yariv, 1992). Minerals of the smectite group are differentiated from talc group by the fact that a small fraction of the tetrahedral Si atoms are substituted by Al atoms, and/or octahedral atoms (Al or Mg) are substituted by atoms of a lower oxidation number. The negative charge per unit cell from isomorphous substitution ranges between 0.5 and 1.3 electron charges. The resulting charge deficiency is balanced by exchangeable cations, mainly Na, Ca, and Mg (Yariv, 1992). The structure of vermiculite is similar (Fig. 2.2.), in which some of the structural Si, Mg, or Al is isomorphically substituted by atoms of a lower oxidation number. Vermiculite usually has greater layer charge density than smectite, and the charge originates mainly from tetrahedral substitution. The negative charge per unit cell from isomorphous substitutions for vermiculite ranges between 1.1 and 2.0 electron charges. The balancing exchangeable cation is Mg, sometimes with a small contribution from Ca or Na. So the nature of the oxygen plane depends on the charge of the silicate layer and on whether the charge results from tetrahedral or octahedral substitution. With no tetrahedral substitution, the oxygen plane is composed predominately of oxygen atoms

belonging to siloxane groups that do not form stable hydrogen bonds with water molecules, and consequently the hydration of this surface is much weaker, and

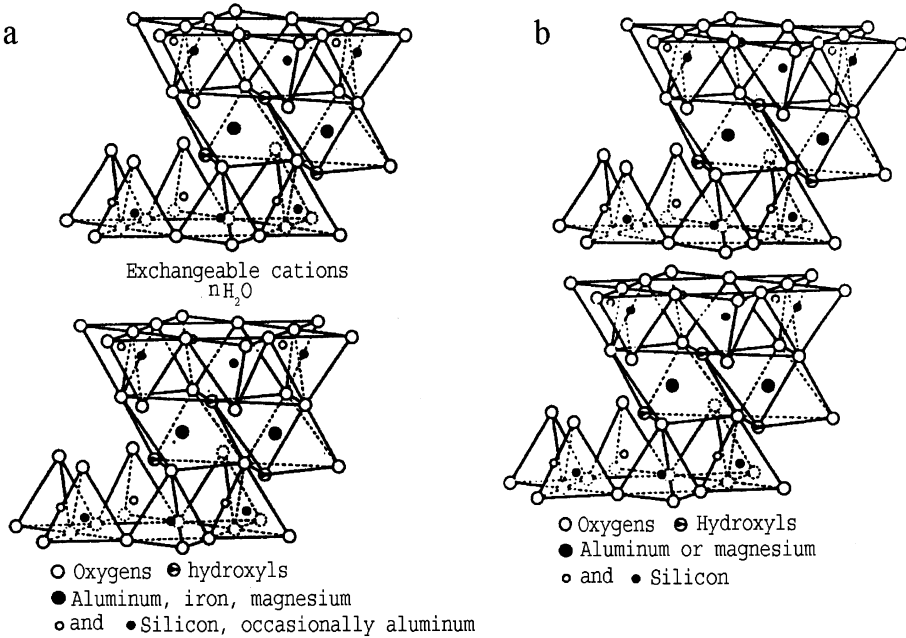


Fig. 2.2. Structure of two groups of layer silicates  
a. expanding TOT clay mineral (smectite or vermiculite);  
b. nonexpanding TOT clay mineral (talc or pyrophyllite)

the surfaces are hydrophobic in nature. With tetrahedral substitution, the oxygen plane is composed of oxygen atoms belonging to Si-O-Al groups that can form hydrogen bonds with water molecules, and consequently the hydration is strong, and the surfaces are hydrophilic to some extent. In addition, the exchangeable cations are also hydrated and have the nature of a “hydrophilic hydration”, and make contributions to the surface hydrophilicity.

Concerning the weakly unsaturated bond crystals, one can take graphite as another example. Graphite forms a distinct layer structure. Within a layer, the carbon atoms are linked through covalent bonds with some metallic bond character, and each atom is surrounded by three nearest neighbours at a distance of 1.418 Å. While the interlayer distance in graphite is large,  $c/2 = 3.354$  Å. Therefore, between the layers there is only weak van der Waals force. As a consequence, graphite cleaves along the (0001) plane, exposing weak van der

Waals bonds, and the interaction of graphite (0001) surface with water consists mainly in dispersion forces, with the possible addition of a hydrogen bonding component arising from interaction of water hydrogen with the p electron cloud of the graphite surface (Schrader, 1992). The water contact angle on a perfect (0001) surface of graphite is  $42^\circ \pm 7^\circ$  (Schrader, 1992). On the other hand, diamond lattice is totally different from graphite. The carbon atoms are held together by strong covalent bonds, and the inter-atomic distance is 1.5445 Å. Diamond cleaves preferentially along the octahedral plane (111) due to the fact that along this plane relatively few bonds need to be broken. The structure of graphite and diamond is shown in Fig. 2.3.

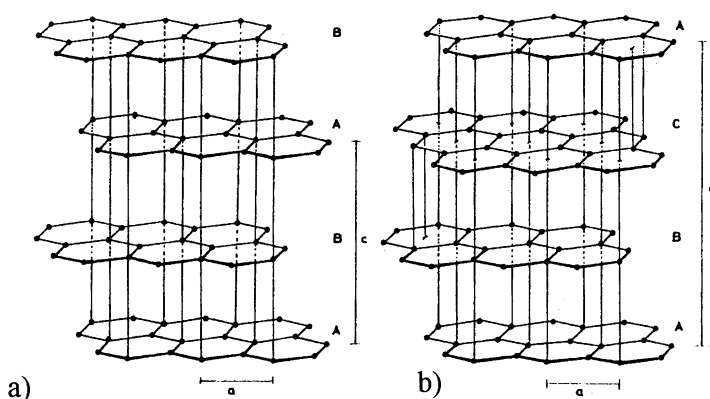


Fig. 2.3A. Structure of hexagonal (a) and rhombohedral graphite (b)

Fig. 2.3B. Structure of diamond C(111)-(1x1)-H, in side view, with H (dark circles) occupying each dangling bond

It is obvious from the preceding discussion that the degree of exposure of crystal lattice points and the strength of the broken lattice bonds can be markedly different depending upon the type of crystal cleavage plane.

Furthermore, let us consider the ion distribution at the surface of ionic crystals. The surface structures of several ionic mineral crystals are illustrated in Fig. 2.4., where the shade denotes the depth of the surface ions, and the numbers reflect the unsaturation degree of surface ion charge (Plaksin and Chapleigina, 1962; Glembotsky, 1980).

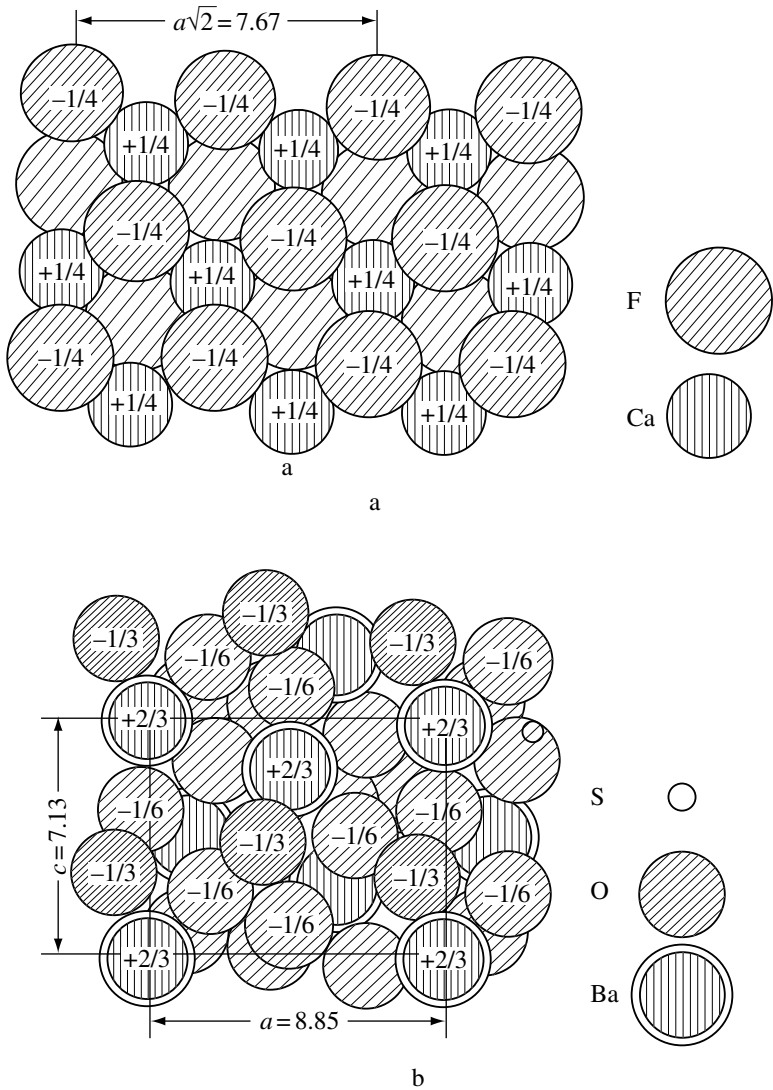
Fig. 2.4(a) shows the (111) plane of fluorite. It can be seen that the charge distribution in the (111) plane is relatively homogenous and that the degree of unsaturation of surface charges is quite low (less than 1/4).

Fig. 2.4(b) gives the (001) plane of barite, the characteristics of the plane are the obvious difference in the surface unsaturation of positive and negative ions and the inhomogeneous distribution of lattice points. A series of “active”



micro regions, where the unsaturation is more than 1/2, are exposed on the surface of barite.

Fig. 2.4(c) shows the (110)(010) planes of cerrusite. The surface of cerrusite is relatively homogenous, the variation of the position of the lattice points in the surface is less than 0.8Å, and  $\text{Pb}^{2+}$  ions are exposed right on or within 0.3Å of the surface, and are not covered by other ions, their unsaturation is relatively high, +2/3.



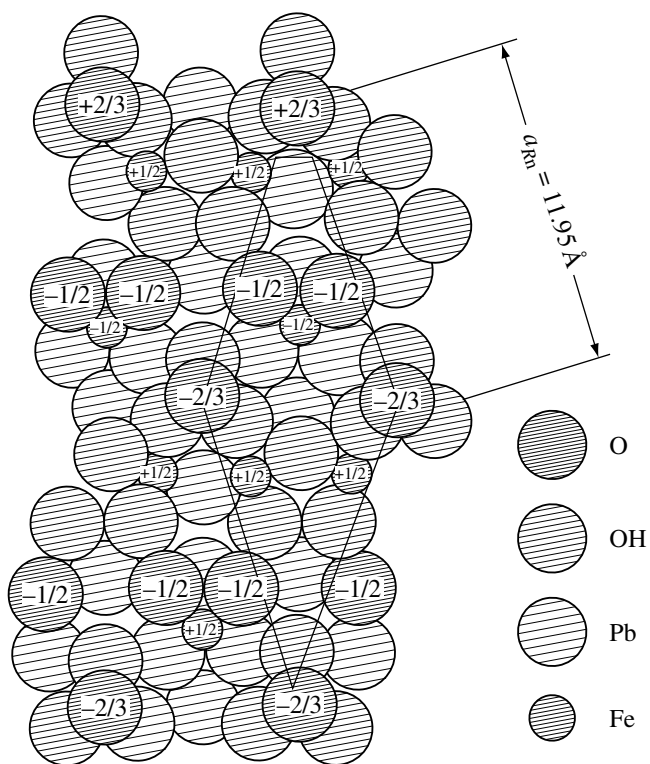
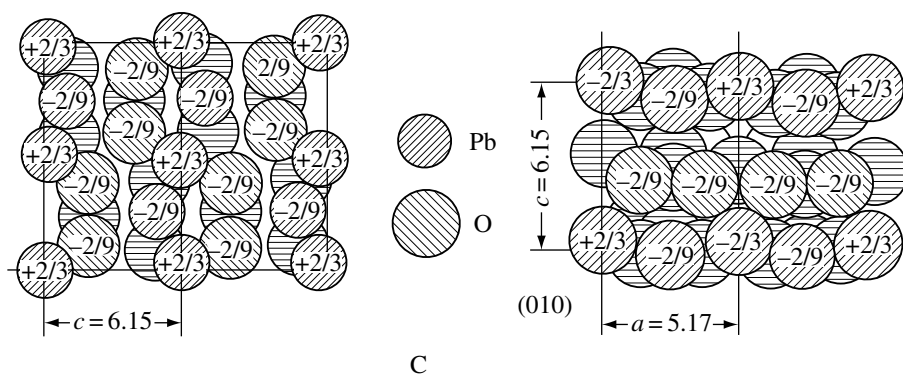


Fig. 2.4. Surface structure of ionic crystals,  
a. Fluorite (111); b. Barite (001); c. cerussite (010); d. Plumbojarosite (1010)

The crystal chemical data of the possible cleavage planes of Cerrusite, estimated by Glimbotsky (1980) are listed in the Table 2.1.

Table 2.1  
Crystal chemical characteristics of cleavage planes of Cerrusite.

Cleavage Plane	Sequence of ion location	Depth of surface Å	Ions	Unsaturation degree of ion
(110)	1		Pb	+2/3
	2	0.3	O	-2/9
	3	0.7	O	-2/9
	4	0.8	O	-2/9
(010)	1		Pb; O	+2/3; -2/3
	2	0.7	O	-2/9
(021) (012)	1		O; O	-2/9; -2/9
	2	0.3	Pb	+4/9

Fig. 2.4(d) and Table 2.2 illustrate the (1010) plane of plumbojarosite (PbFe<sub>6</sub> (OH)<sub>6</sub>(SO<sub>4</sub>)<sub>3</sub>). It can be seen that the distribution of the lattice points is extremely inhomogeneous in the plane level as well as in the depth of surface. Pb<sup>2+</sup> ions are deeply distributed at the arrangement level 12, therefore their unsaturation degree is very low (+1/6). Comparing with Pb<sup>2+</sup> ions, Fe<sup>3+</sup> are located closer to the surface (2.15Å) than Pb<sup>2+</sup> (3.7Å), and their unsaturation (+1/2) is much higher. That is the reason why plumbojarosite possesses the similar surface properties of iron minerals.

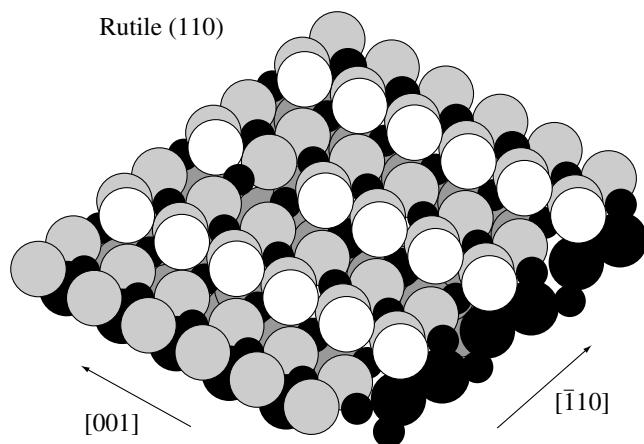
Table 2.2  
Crystal chemical characteristics of plumbojarosite (1010) plane

Sequence of ion location	1	2	3	4	5	6	7	8	9	10	11	12
Depth of surface, Å		1	1.7	1.85	2.1	2.15	2.2	2.5	2.7	3.1	3.35	3.7
Ion	O	2(OH)	(OH)	O	O;O	Fe	O;O	O	(OH)	O	2(OH)	Pb
Unsaturation degree of ion	-2/3	-1/2									+1/2	+1/6

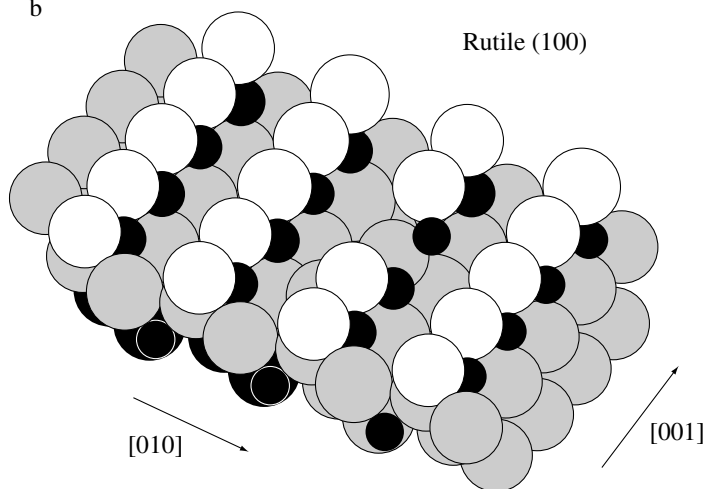
Rutile has three possible cleavage planes: (110) (100) and (001) (Henrich and Cox, 1994). Models of these surfaces are shown in Fig. 2.5a, b, and c. However, the cleavage plane in rutile is preferentially along(110), because it can reduce the nearest-neighbor ligand coordination of the surface cations by the smallest amount. It can be seen from figure that the (110) surface is not atomically flat, row of ‘bridge’ O ions lie above the main surface plane, which contains equal numbers of five- and six-fold coordinated cations. Compared to (110), all of the cations on (100) are five-fold coordinated with O ligands, while

on the (001) surface the nearest-neighbor ligand coordination of the surface cations has been reduced from six to four, it leads to a very high surface energy for (001) of rutile, the calculated value is twice as large as that for (110) of rutile.

a



b



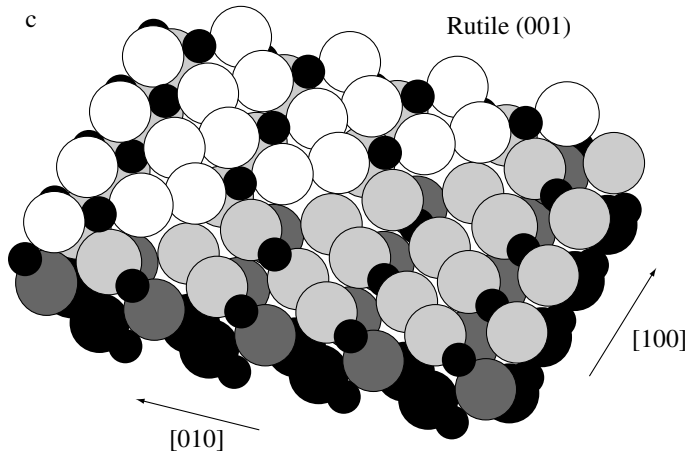


Fig. 2.5. Model of rutile surface:

- a. (110) surface, two types of O-vacancy defect are shown;
- b. (100) surface, showing one surface O-vacancy defect;
- c. unrelaxed (001) surface, showing a step to another (001) terrace

From the preceding discussion it is clear that the strength of an unsaturated bond on the crystal surface mainly depends on the crystal-chemical characteristics of solid particles such as the lattice type and the direction of cleavage planes, etc. Furthermore, even in the case of the same type of bonds, such as ionic bonds, they may have different behavior or different bond strengths due to different ion situation on the plane: different distribution depths and different unsaturability as well as the difference of the other surface ions covering them.

Moreover, it is worth mentioning that self-saturation may succeed after a strong ionic-covalent bond has been broken. The interaction among surface neighboring atoms or ions causes the broken bond to be balanced to a certain degree (Bogdanov, 1974). For instance, the surface atoms can capture the electrons from the neighboring atoms or ions to reduce their unsaturation (Barskii et al, 1979). This phenomenon is often observed in the case of sulfide crystals and is the main cause of observed slight natural hydrophobicity of sulfides.

### 2.1.2. SURFACE ENERGY AND SURFACE FREE ENERGY (SURFACE TENSION)

A cleavage of continuum crystal structures causes the surface atoms or ions to be subjected to an asymmetrical force field action which results in an excess energy corresponding to the bonding energy of the crystal lattice. Hence, breaking crystals and exposing fresh surfaces requires work. At a constant

pressure and temperature, the reversible work spent in producing a unit area of fresh surface is termed the surface free energy  $A_s$ . If the stretch tension, which may also occur during crystal breakage, is negligible, the solid-surface free energy  $A_s$  and surface tensions can be treated as equivalent. Thus

$$A_s = \gamma = \left( \frac{\partial G}{\partial A} \right)_{T,P} \quad (2.1)$$

On the basis of the surface thermodynamics, the enthalpy of unit surface can be expressed as

$$H_s = E_s + \underbrace{(PV)}_0 = A_s + TS_s \quad (2.2)$$

where,  $T$  is temperature;  $E_s$  the total surface energy;  $S_s$  the surface entropy. For the surface of solid crystals,  $PV$  can be negligible, so the surface energy  $E_s$  equals the surface enthalpy  $H_s$ , i.e.

$$A_s = H_s - TS_s \quad (2.3)$$

$$\text{or } A_s = E_s - TS_s \quad (2.4)$$

at a constant pressure, the surface entropy  $S_s$  can be related by

$$S_s = - \left( \frac{\partial A_s}{\partial T} \right)_P = - \frac{d\gamma}{dT} \quad (2.5)$$

The relationship between the total surface energy  $E_s$  and the total surface tension  $\gamma$  then takes the form

$$E_s = \gamma - T \frac{d\gamma}{dT} \quad (2.6)$$

With regard to most liquids, the surface tension decreases in linear fashion along with the temperature drop. For example, the water interfacial tension  $\gamma = 72.75 \times 10^{-3} \text{ J/m}^2$  at  $20^\circ\text{C}$ , and  $d\gamma/dT = -0.16$ , thus in accordance with Eq. (2.6) the total surface energy  $E_s = 120 \times 10^{-3} \text{ J/m}^2$ . However, it is difficult to measure the surface energy  $E_s$  and the surface free energy  $A_s$  (or surface tension  $\gamma$ ) of solid crystals directly by experiments. An analysis of the available data of solid crystals suggests that in most cases values of  $E_s$  and  $A_s$  are closer to each other. For instance,  $A_s$  of NaCl equals  $0.23 \text{ J/m}^2$  while  $E_s$  equals  $0.29 \text{ J/m}^2$ .  $A_s$  and  $E_s$  of magnesium oxide (MgO) is  $1.00 \text{ J/m}^2$  and  $1.09 \text{ J/m}^2$  respectively,

whereas both  $A_s$  and  $E_s$  of diamond are  $5.6 \text{ J/m}^2$  (Fuerstenau and Raghavan, 1976). Consequently, in certain cases, the three values: the surface energy, the surface free energy and the surface tension of solid can be accepted as the same.

As noted in Section 2.1.1, the factors, such as the difference in the ionic or atomic density, the distribution and coordination number (corresponding to unsaturability of the surface ions) and the distances between ions or atoms in cleavage plane, may cause obvious differences in the surface energy of various cleavage planes of crystal. Theoretical calculation of the surface energy of the typical covalent bond crystal – diamond demonstrates (see Fig. 2.6) that at (111) cleavage plane of diamond three bonds of unit crystal cell are broken, the distance between (111) planes is  $0.232 \text{ nm}$ , the density of diamond is  $3.51 \text{ g/ml}$  and the bond-density per unit area calculated is  $1.83 \times 10^{15} \text{ bonds/cm}^2$ . If the bond energy is assumed as  $90 \text{ kcal/mol}$ , the calculated surface energy for (111) plane of diamond is  $5.65 \text{ J/m}^2$ . Whereas the surface energy of the (100) plane calculated by the same way is  $9.82 \text{ J/m}^2$ .

The surface energies of the different crystal planes of the haloids of basic metals are illustrated in Table 2.3 (Eadington, 1977).

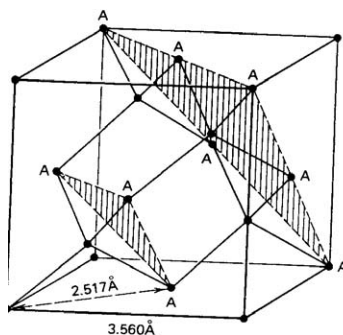


Fig. 2.6. Diamond structure, showing different distances between cleavage planes (From Adamson, 1990)

Obviously, in order to characterize crystal surface, it is also important to know the fractions of every cleavage plane. Electron micrographs showed the presence of the (100), (010), (001) and (021) planes on a needle shaped goethite crystal. The surface of goethite consists of about 90% (110) face and 10% (021) face. Thus, the main crystal plane of goethite is the (110) face, and this face is dominated by triply coordinated surface  $\text{Fe}_3\text{O}(\text{OH})$  groups (Hemstra et al., 1996). Whereas for rutile the (110) and (100) faces are the dominant ones (Henrich and Cox, 1994; Jones and Hockey, 1971).

Table 2.3

Surface energy of different crystal planes of haloids

Haloid	$E_s, \text{ J/m}^2$	
	(100)	(110)
LiF	142	568
LiCl	107	340
NaF	216	555
NaCl	158	354
NaBr	138	304
NaI	118	252
KCl	141	298
RbCl	138	277

### 2.1.3. EDGE ENERGY AND ANGLE ENERGY

The surface tension of solids can also be calculated using the following simplified approach by assuming that the bonding energy between the most neighboring atoms in crystal lattice is  $E$ , the coordination number is  $k$ , the total number of atoms in crystal is  $n$ , the dimension of the crystal to be large enough compared to its atoms, and the distance between neighboring atoms is  $a$ . Then, the total bonding energy  $H$  (or named condensation energy) can be evaluated by:

$$H = \frac{nKE}{2} \quad (2.7)$$

In breaking solid, the energy  $A_s$  or  $\gamma$  of the unit fresh surface is

$$A_s = \gamma = \frac{E}{2a^2} = \frac{H}{nKa^2} \quad (2.8)$$

Eq. (2.8) tells us again that a value of surface energy relies on the geometric shape of the crystal cleavage plane and the position of the surface atoms. Because the coordination number  $K$  of the atoms at edges and angles is lower than that of the atoms in steps of surfaces, the surface edges and angles possess more energy and are more active. The bonding energy values of ions on the cubic ionic lattice surface are given below (Alexandrovich, 1983).

The plane surface free energy  $0.0662 \text{ e}^2/a$

The edge surface free energy  $0.0903 \text{ e}^2/a$

The angle surface free energy  $0.249 \text{ e}^2/a$

where  $e$  is the charge of electron, and  $a$  is the distance between neighbouring ions.

It is evident that an unsmooth broken surface has more edges and angles and hence is more active. The finer the particles the larger is the fraction of its edge and angle energy in the total surface energy. The values of surface energy



and edge energy of different dimensional particles of NaCl are exhibited in Table 2.4 (Adamson, 1990).

Table 2.4

Dimension of NaCl and its surface and edge energy

Edge length mm	Number of particles	Total surface area, m <sup>2</sup>	Total edge length, m	Surface energy J/kg	Edge energy J/kg
7.7	1	$3.6 \times 10^{-4}$	$9.3 \times 10^{-2}$	$1.08 \times 10^{-1}$	$2.8 \times 10^{-10}$
1	$4.6 \times 10^2$	$2.8 \times 10^{-3}$	5.5	$8.4 \times 10^{-1}$	$1.7 \times 10^{-8}$
$1 \times 10^{-1}$	$4.6 \times 10^5$	$2.8 \times 10^{-2}$	$5.5 \times 10^2$	8.4	$1.7 \times 10^{-6}$
$1 \times 10^{-2}$	$4.6 \times 10^8$	$2.8 \times 10^{-1}$	$5.5 \times 10^4$	$8.4 \times 10^1$	$1.7 \times 10^{-4}$
$1 \times 10^{-3}$	$4.6 \times 10^{11}$	2.8	$5.5 \times 10^6$	$8.4 \times 10^2$	$1.7 \times 10^{-2}$
$1 \times 10^{-5}$	$4.6 \times 10^{17}$	$2.8 \times 10^2$	$5.5 \times 10^{10}$	$8.4 \times 10^4$	$1.7 \times 10^2$

Notes: It is known that for NaCl  $E_s = 0.15 \text{ J/m}^2$ ,  $E_{\text{edge}} = 3 \times 10^{-10} \text{ J/m}$

#### 2.1.4. INHOMOGENITY OF PARTICLE SURFACE

##### 2.1.4.1. Displacement of surface atoms

The discussion above deals with the variations of surface energy of the different cleavage planes of ideal crystal and the difference of surface energy at different positions on the same plane. The further discussion, then, refers to another factor which causes the additional deviation of surface energy from the ideal values - displacement of the surface atoms of crystal.

It has been observed that fresh surface atoms will not exactly remain at their original lattice position. The surface atoms, instead, will definitely displace somewhat in the parallel or vertical directions of the crystal surface. The former is termed rearrangement and the latter relaxation (Morrison, 1977). The rearrangement and the relaxation of surface atoms can increase the bonding energy of them with other atoms in the lattice. Unsaturation of surface atoms will thus be reduced somewhat and the total surface free energy is decreased to some extent.

Fig. 2.7 illustrates the relaxation phenomenon of  $\text{Na}^+$  and  $\text{Cl}^-$  in a cleavage (100) plane of NaCl (Verwey, 1946; Weyl, 1952; The Society of Chemical Engineers, Japan, 1975). Fig. 2.7(a) is the ideal crystal plane, Fig. 2.7(b) shows the polarization of  $\text{Na}^+$  and  $\text{Cl}^-$ , their induced dipole moment as well as the forces acting on them vertical to the plane affected by the lattice ions also differ. Fig. 2.7(c) shows that  $\text{Na}^+$  with weak polarization displaced to the inner part of the lattice and the positive charge ends of more polarized  $\text{Cl}^-$  strongly repelled by positive ions in the lattice displace to the outer areas of the lattice. As a result, this displacement shortens the distance between the surface  $\text{Na}^+$  and the lattice (from  $2.81 \text{ \AA}$  to  $2.66 \text{ \AA}$ ) and on the other hand enlarges the distance between the surface  $\text{Cl}^-$  and the lattice (Fig. 2.8).

Low-energy electron diffraction (LEED) studies showed that sphalerite undergoes considerable relaxation of surface atoms (Vaughan et al., 1997). This relaxation involves movement of the Zn atoms in towards the bulk and S atoms outwards, with displacements of the order of  $< 0.5 \text{ \AA}$  in the outermost layer and  $0.14 \text{ \AA}$  in the second layer.

In addition, the rearrangement of surface atoms can also result in some overlapping or unsaturated bonds.

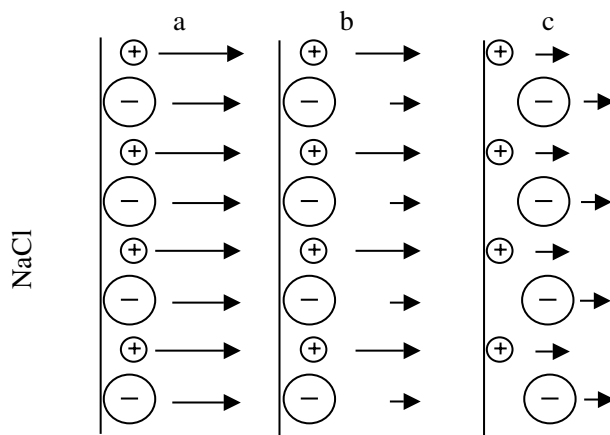


Fig. 2.7. Electronic deformation and ionic rearrangement at NaCl surfaces (after The Society of Chemical Engineers, Japan, 1975)

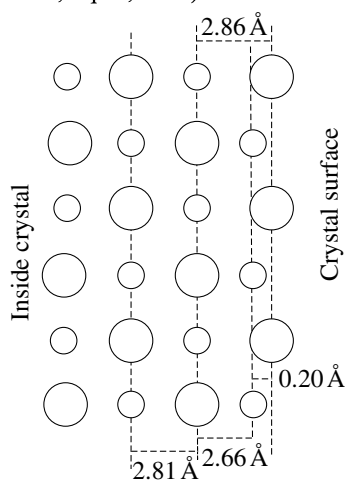


Fig. 2.8. Real structure of NaCl surface (after The Society of Chemical Engineers, Japan, 1975)

#### 2.1.4.2. Surface defects of crystal

In most cases, the crystal surfaces including not only fracture but also cleavage plane are irregular. Even though cleavage planes like that of mica commonly considered to have a smooth surface, various steps of 2-100 nm height can be observed by means of the instruments with high resolution power, e.g. electron microscope (Gragg, 1961).

When an actual crystal is broken along a plane, the defects, such as micro-boundaries, edges, steps, splits, screw dislocations, vacancies and interstitial atoms emerge in the broken surface of the crystal. Fig. 2.9 (Flood, 1967) shows the typical situation of different defects of the surface of cubic crystal in which the little cube stands for atoms in the crystal. In the figure, 1 denotes the position of a normal atom; 2 and K denote the atoms located at the step and the edge of the step (or named kink), respectively; 3 and 4 the self-adsorbed crystal atoms at the surface and steps respectively; 6 the vacancy in the step left by crystal atom migrated away; 7 the surface step caused by the emergence of the screw dislocation (the initial and final positions can be found in the figure); 8 the final position of an edge dislocation in the surface; black balls in the figure denote absorbed atoms; 9, 10, 11 and 12 denote the absorbed atoms separately in the crystalline surface, on the steps, at the kink and in the vacancies; 13 stands for the state of co-adsorption of foreign atoms and crystal atoms.

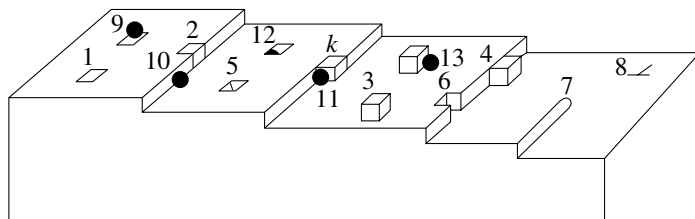


Fig. 2.9. Different defects of cubic crystal surface

Recently, the scanning probe microscopies, such as electron tunnelling spectroscopy (ETS), both vacuum- and air/liquid-based scanning tunnelling microscopy (STM), and air/liquid-based atomic force microscopy (AFM) are applied to mineral surface examination. In addition, many of the most important vacuum-based surface-sensitive techniques are also applied to study mineral surface. These include X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS, respectively), Auger electron spectroscopy and scanning Auger spectroscopy (AES and SAM, respectively), secondary ion mass spectroscopy (SIMS) and related techniques, Rutherford backscattering spectroscopy (RBS) and resonant nuclear reaction (RNR) analysis, scanning and transmission

electron microscopy (SEM and TEM, respectively), and low energy electron diffraction (LEED). Due to the application of these modern experimental methods for particle surface characterization, the images of real crystal surfaces at atomic or near-atomic resolution become available (Hochella, 1990). Fig. 2.10 shows a STM (Scanning Tunnelling Microscopy) image of a galena cleavage surface (001), Fig. 2.11 is a model of the galena (001) surface with one atomic step, showing a S and Pb vacancy on it. Fig. 2.12 shows an atomically-resolved STM image of the same plane, in which the S vacancies and the atomic step in the lower left corner are demonstrated clearly. Fig. 2.13 shows an STM image of the (001) surface of hematite (Hochella, 1995), showing sites with  $3\text{\AA}$  periodicity, as expected for the relaxed surface oxygen array.

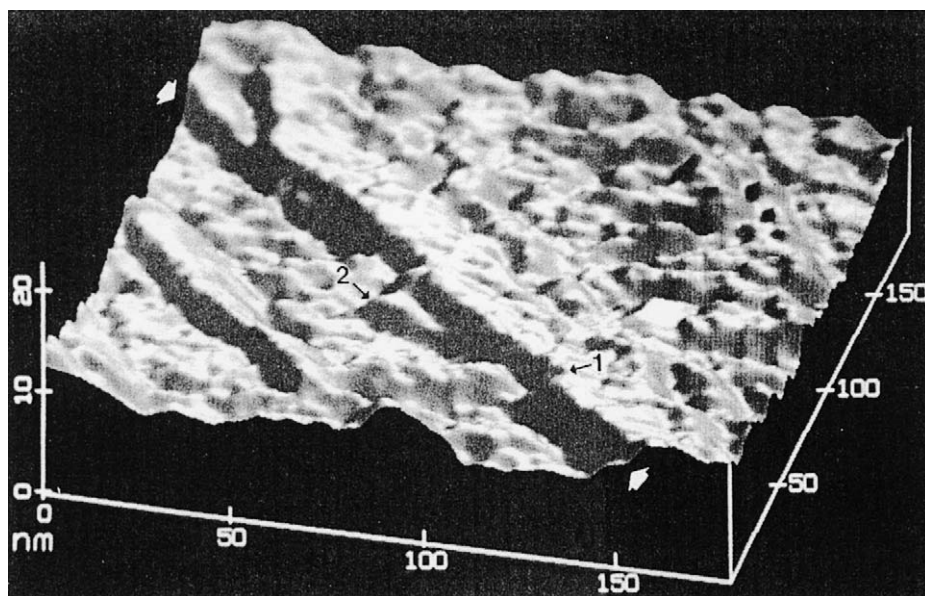


Fig. 2.10. STM image of a galena cleavage surface (001), showing moderate vertical exaggeration. The wide arrows marks a cleavage step 30 to 50  $\text{\AA}$  in height. Also denoted are a kink site (labeled 1) and a half-step protrusion (labeled 2) Hochella, 1990).

It can be seen from Fig. 2.10 that the (001) cleavage surfaces of galena are not flat, there are steps varying from 30 to 50  $\text{\AA}$  in height along the step, several kink sites (point 1) and protrusions from the step (point 2). In Fig. 2.12 several S vacancies and an atomic step in the lower left portion of the image are clearly observed.