

Atoms and Crystals¹

X. Oudet,

Fondation Louis de Broglie,
23, rue Marsoulan, 75012 Paris, France
xavier-oudet@wanadoo.fr

ABSTRACT. The interpretation of some crystal structures is based on Dirac's atom in a corpuscular approach. This conception allows completing the Bohr-Sommerfeld approach with the comprehension of the doublets. It exhibits the existence of windows open on the nucleus allowing bonds with the electrons of the neighbour atoms. As a result this sheds light on the valence notion which allows describing the interatomic bonds, each atom having an attracting role with the nucleus and its outermost electrons.

1 Introduction

The diffraction of X-Rays, neutrons and electrons has allowed us to describe numerous crystal structures, on the other hand the absence of a clear interpretation of the quantum mechanics in particular of the doublets has miss us of the understanding of the structures from that of the atom. The interpretation of the magnetic moments of numerous metals and compounds in the framework of Dirac's model supposing that each electron behave like in a hydrogen atom, allows identifying the magnetic state of each additional electron of the 3d or 4f shell, [1]. This identification leads to the sharing of the states between the two subshells of a same shell giving the doublets; either 2ℓ for the first or $2(\ell + 1)$ for the second. Thus we find again the Runge law established in 1907 interpreting anomalous Zeeman Effect for metals in a gaseous state as sodium or zinc [2].

These results suggest the possibility to attribute the difference of levels of the doublets to a small difference of inert mass hypothesis suggested by the emission and the absorption of photon during the transitions between two levels. In this goal the matter of the proton and the electron is supposed built of grains with much more small dimensions. With this hypothesis we have proposed to interpret the wave function of Dirac as representing the density of matter in such a way that the different derivatives represent the mechanical action generate by the motion of the electron in the meaning of the classical mechanics [3]. This interpretation shows the value of the model of Bohr-Sommerfeld; to make it more complete one has to consider that the quantum of action traditionally associated to the rotation of the electron, equally

¹ This is the English version of the French work: "Atomes et cristaux ", published in: Ann. Fondation Louis de Broglie, **32**, 77-114, (2007).

include a parallel translation to that of the axis of rotation. Supposing the equipartition of the energy, therefore of the masse, these two degrees of freedom are supposed to share into two equal quantities the quantum of action which generate them giving that was called the space quantification and giving the half values of magnetic moments often observed.

This approach of the hydrogen atom allows describing the motion of the electron around the proton, then for the atom with several electrons, the structure of the atomic space. With the knowledge of the atomic space it is then possible to understand the building process of the crystal space. In space structure one has to understand the spacio-temporal relations of the electrons of the atom, then the spacio-temporal inter-atomic relations giving access to the crystal space.

To tackle this subject we will rely on the study "Crystal Structure and Bonds" published in 1983 [4] and supported by several works. The discovery of the high T_c superconductors has been rapidly followed by that of the 2p holes on oxygen ions giving support to the hypothesis of defect of ionicity on atoms of oxygen taken in this first work with the study of the La_2O_3 structure. This discovery of the oxygen 2p holes and that older of the rare gas compounds have finally led us to propose a model of neutral atoms [5] for all the ionic compounds. Thus it matter to understand the chemical bond itself with neutral atoms. The clue has to be found in the spatial distribution of the electrons of an ns , np , nd and nf shell itself. The goal of this study is to show that this distribution allows all the atoms to be able to attract the outer electrons of the neighbour atoms with a more important power for metal than metalloids. As a result it shed light on diverse properies of bonds in crystals.

The place of an atom in the periodic table of the elements being the synthesis of a great number of their properties we will start to recall in section 2 some quantum properties. The section 3 will devoted to the description of the spatial distribution of the electrons contributing to bonds between neighbour atoms. The section 4 will recall the synchronous bond connected to the periodic motion of the electrons. The section 5 will introduce the disorder as a component of the crystal state and will tackle the notion of valence. The section 6 will tackle some structural crystal interpretations. The section 7 will propose some remarks as a conclusion.

2 The periodic table and the quantum numbers

It is in 1869; February 17 that Mendeleev was distributing to numerous chemists its system of classification of the elements [6]. It was the discovery of the quantum properties of the electrons in the atoms which was allowing the understanding of the organization. It was first the works of Moseley which, from the study the frequency of the X-Rays, brought important results supporting the notion of atomic number. A very comprehensive account on the spectroscopy and quantum mechanics can be found in the reference book of White « Introduction to Atomic Spectra » with a great number of results and references concerning the spectral lines, the quantum mechanics and the periodic table [2]. After the atomic number it was the discovery of numerous spectral lines of Balmer (1885), Rydberg, Paschen to just quote the more known. These researchers showed the role of an integer number in the variation of the frequency of the corresponding lines. Thanks to Bohr work (1913) this number was going to become the principal quantum number n having a close connection with the different rows of the periodic table. Then the works of Sommerfeld (1916) have allowed understanding the classification of the series in sharps s , principals p , diffuses d and fundamentals f corresponding to the secondary quantum numbers ℓ also call orbital which is associated to the momen-

tum of the quantum state. Those numbers explained by the same token the different columns of the table. Except the shells ns , those shells are divided into two subshells as indicate by the double spectral lines and as Table 1 and Table 2 recall it. The Sommerfeld approach did not allowed understanding the origin of this division. It was Dirac approach which allowed solving this difficulty; it shows that there are two types of lightly different states for the same number of quanta of rotation. Finally each element corresponds to an additional proton and electron in comparison to the previous element. To each additional electron corresponds a distinct magnetic state characterized by the m quantum number which is specific of the element [1].

Table 1. The different quantum numbers in Dirac's model, their relation of order and ν the number of states of the subshell; the type II correspond to the first subshell and the type I to the second. The principal n , orbital ℓ , radial r , magnetic m quantum numbers; le number ρ is introduced in the degree of the polynomials defining the radial functions component of the solutions of the equation of Dirac. To avoid any mix-up with the np shells giving doublets we use the Greek letter ρ instead of the letter p used by Louis de Broglie [8], [3]. The limits of the m number result of the study of the solutions of the equation of Dirac and are experimentally confirmed with the measurements of the magnetic moments [1].

$n \geq 1$	$\ell \leq n-1$	$r \leq n-1$	$n = \ell + r + 1$	ν
Type II ; first subshell	$k = \ell$	$\rho = r + 1$	$-(\ell-1) \leq m \leq \ell$	$2(\ell-1)$
Type I ; second subshell	$k = -\ell - 1$	$\rho = r$	$-\ell \leq m \leq \ell + 1$	2ℓ

However it matter to underline the reversal of situation in the case of the rare earths elements, that is those corresponding to the filling of the $4f$ shell. Indeed if the periodic table has been established before the discovery of the different quantum states and confirmed with it, they are mostly the theoretical works of Sommerfeld and Dirac which have allowed lining up the $4f$ elements. Without these works we would be in difficulty to line up the $4f$ elements on the basis of their chemical properties, as Mendelejev done for the others elements. Let us recall that at the time of the publication of the periodic table in 1869 very few elements of the rare earths had been isolated, to see for example the genealogical table of their discovery [7]. This fact comes from their very similar chemical properties making their separation very difficult. We will see (5.2) thanks to the special properties of the $4f$ electrons, how and why these elements have a great similarity of chemical properties.

Table 2. The s, p, d, f shells and the corresponding subshells.

$s ; \ell = 0$	$p ; \ell = 1$		$d ; \ell = 2$		$f ; \ell = 3$	
$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2} ;$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$
$k = -1$	$k = 1$	$k = -2$	$k = 2$	$k = -3$	$k = 3$	$k = -4$

Now what about the division into subshells of the np, nd and nf shells. We know that it explains the doublets of some spectral series. The division in subshells of the $3d$ and $4f$ shells is clearly put in view with the magnetic properties of these elements [1], [9]. By analogy of

position in the classification it is transposed into the others shells. Concerning the elements *ns* they correspond to second subshell, the first one does not exist in their case.

3 The spatial distribution of the *ns*, *np*, *nd* and *nf* shell.

To understand the role of the subshells in the chemical bond let us first consider each electron in a hydrogenous atom and define the atomic space. Consider the frame of reference Ox, Oy, Oz , where O is the atomic nucleus centre of potential. To introduce the symmetry of the intrinsic rotation we suppose the corresponding axis parallel to Oz . Consider G the plane of the motion containing the Ox axis by construction and E the equatorial plane containing the axes Ox and Oy . Let E be the energy and p the momentum of the electron upon an interval dt of time and dl of space along the trajectory; the action $pdl = Edt$ associated to the motion upon this interval dt, dl has two components parallel to the equatorial plane E and the third to Oz . The plane G of the motion cut the equatorial plane along Ox . The point B is one out of the two points where the trajectory pierces the plane E (Figure 2). The properties of the atomic space are defined according to those of the proton and the electron. The proton being much heavier than the electron, it is the motion of the electron around the proton that one has to describe. Let α be the angle between the motion plane G and the equatorial plane E perpendicular to the axis Oz and to that of the intrinsic rotation, it plays an important role into the structure of the atomic space.

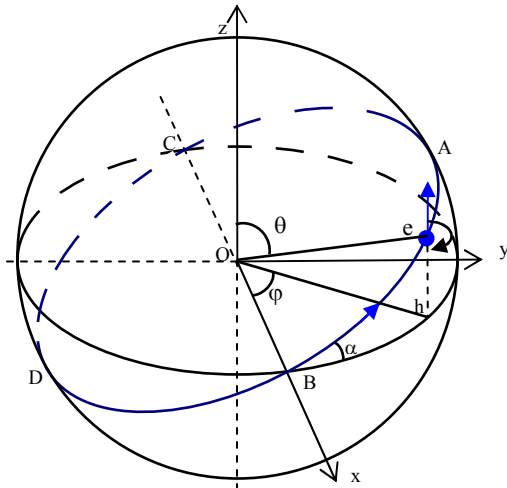


Figure 1. The motion of the electron. The point O is the centre of the potential, the plane of the motion $ABCD$, the equatorial plane Ox, Oy . In e the electron along its trajectory.

ular to the axis Oz and to that of the intrinsic rotation, it plays an important role into the structure of the atomic space.

The magnetic properties of the atom in a solid point out for each electron a moment equal to that it would has in a hydrogen atom [1]. For a gas in a magnetic field the same property is exhibited through the Runge law [2]. As a result the angle α between the motion and equatorial plane stay the same whatever be the number of electrons of the atom. This angle depends only of the quantum state. On the other hand the radial action $p_r dr$ does not modify the orientation of the circular trajectory of basis. Thus one has just to determine α for these states. Consider a small movement $d\ell$ along the trajectory. The corresponding rotation is $rd\phi$. The component $p_\phi rd\phi$ of the action parallel to the equatorial plane E is the product of the projections of the displacement and of the momentum.

Thus:

$$\cos^2 \alpha = \frac{p_\phi r d\phi}{p d\ell} \quad (3.1)$$

During one period $\int p_\phi r d\phi = u$ where u is the atomic momentum in respect to Oz , we have $u = m^{-1/2}$. In Dirac's theory the momentum around Oz is not the classical moment Mz but the momentum $Nz = Mz + Sz$ where Sz is the operator introducing the intrinsic rotation and the half-integer values [8]. The study of the solutions of Dirac's equation shows that the maxi-

num of u then of $m - \frac{1}{2}$ for the first subshell is lower of one unit to that of the second subshell, moreover for each value $u(m)$ there is a value $u = -u(m)$; as a result there are two missing state in the first subshell in respect of the second, the interpretation of the experimental magnetic moments confirms these values.

It is this aspect of the quantum mechanics which is essential. To interpret this fact let us consider the rest mass m_0 of the electron and distinguish active masse m_a , representing in absolute value, the kinetic energy of the motion and the inert mass m_i such that $m_a + m_i = m_0$ [3]. Let W be the energy of the motion, we have:

$$m_i = Wc^{-2} \quad \text{with} \quad E = W - m_0c^{-2} \quad \text{it comes} \quad m_a = -Ec^{-2} \quad (3.2)$$

Why there are two missing states in the first subshell? If we admit that the inert mass of the electron is variable during its motion then the two missing states in the first subshell can correspond to a quantum of action generated by a small variation of the active mass. Indeed suppose that the higher active mass belongs to the states of the first subshell, the electron in motion with an active mass lightly higher than to that of the second subshell generate a number of quanta ρ higher of one unite to those of the second [10]. For the same orbital quantum number ℓ , it is no longer able to stabilize one of the two state corresponding to the maximum orbital momentum that it can takes in the second subshell.

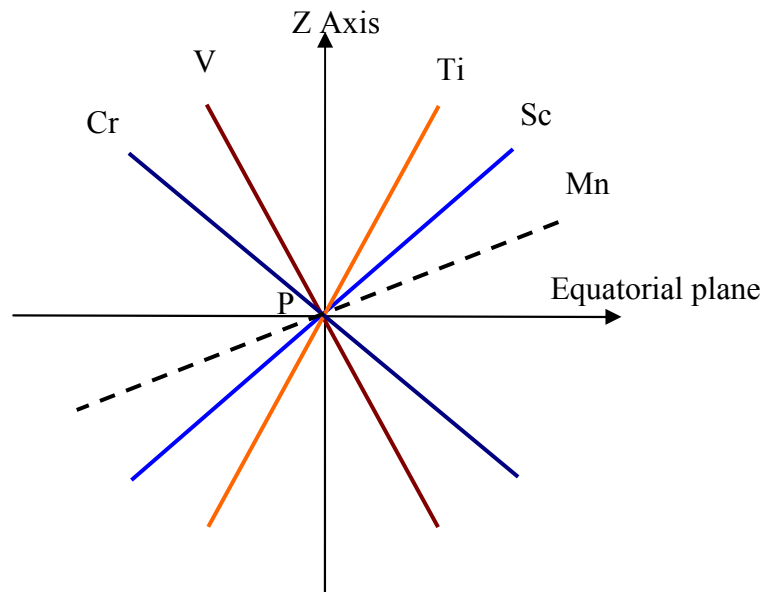


Figure 2. The spatial distribution of the electrons $3d_{3/2}$ and the angular azimuthal position of the additional electron of the manganese occupying the first $3d_{5/2}$. The electrons are supposed to orbit in perpendicular planes to that of the figure. The angle between the equatorial plane E and the plane of gravitation G is that given by the relation (3.3), its sign is that of u .

Consider the orbital action of rotation A_{Or} during one period. To the unit of action corresponding to the intrinsic rotation, it can have ℓ additional unit of action of rotation, the sum of the both giving the orbital action of rotation $A_{Or} = (\ell + 1)$. The rotation is assumed by the intrinsic rotation, the number ℓ can take the zero value in this case the states correspond to those

of the second subshell. With the orbital action $A_{Or} = (\ell + 1)$ but for an active mass very lightly higher to that of the states of the second subshell [10], when ℓ is higher than zero, the unit of intrinsic rotation can be included in the quanta ℓ . There are the states of the first subshell.

This remarks show that the values of $\cos^2\alpha$ (3.2) are given for the both subshells by the same expression; it comes:

$$\text{Cos}^2\alpha = \left| \frac{u}{\ell+1} \right| = \left| \frac{m - \frac{1}{2}}{\ell+1} \right| \quad (3.3)$$

The interpretation of the magnetic moments shows that the first occupied quantum state of a subshell is that having the greatest orbital contribution of rotation $m = |k|$ that is $m = |k| = \ell$ for the first subshell and $m = |k| = (\ell + 1)$ for the second [1]. We find again this difference of one unit between the two maximums of m . It is this difference which comes, by hypothesis, from the fact for the first subshell the increase of one quantum, by comparison to the previous shell, is obtained by an unit modifying the mass of the electron since that for the second subshell the increase modifies the kinetic quantum number k . Thus the orientations of orbiting planes of the different quantum states in each subshell having same value of u are the same, but the two states of the first subshell, corresponding to the values $u(\ell + 1)$ et $u(-\ell) = -u(\ell + 1)$ (see appendix in [3]), are missing. On the other hand as we have underlined it to each electron having a momentum u corresponds another electron with the momentum $-u$. We will say that they make a couple of twins.

Table 3. The twin elements for the circular states, the azimuthal angle α of plane of motion on the equatorial plane and the polar angle β between the axis Pz and the closest states from this axis.

Shells	1s	2p		3d			4f			
1 st subshell			B C		Sc Cr	Ti V		La Sm	Ce Pm	Pr Nd
2 nd subshell	H He	N O	F Ne	Mn Zn	Fe Cu	Ni Co	Eu Yb	Gd Tm	Tb Er	Dy Ho
α	45	30	60	24.1	45.0	65.9	20.7	37.8	52.2	69.3
β	45	30		24,1			20,7			

This difference between the first and the second subshell is fundamental because it allows explaining the ionic bond with neutral atoms that we tackle in the section 3.2. The Figure 2 symbolizes this situation for the 3d shell where the manganese is the first element with an electron $3d_{5/2}$. The Table 3 gives the distribution of the 1s, 2p, 3d and 4f elements in the two corresponding subshells. The sharing giving this distribution is done at the same position of the periodic table for the elements of higher atomic number.

Spatial intra-atomic Orientation.

To complete this analysis one has to discuss, for a filled subshell, the orientation of the different twin couples between them. On the Figure 2 we have given the azimuthal angular orientation of the different electrons of the $3d_{3/2}$ subshell. For simplicity this representation is

given as if all the planes of motion of a twin have the same straight line of intersection in the equatorial plane and perpendicular to the plane of the Figure 3 and including the potential centre P. Consider for example the twin couple scandium, chromium that is {Sc, Cr} on the Figure 2. The two orbiting plane of the $3d_{3/2}$ electrons of such a couple have their intersection CD in the equatorial plane (Figure 3). For the orbiting planes of the $3d_{3/2}$ electrons of the titanium, vanadium twin that is {Ti, V} in the $3d_{3/2}$ subshell the interaction of repulsion make that they intersect, in the equatorial plane or in its vicinity, along a straight line perpendicular the straight line CD of the $3d_{3/2}$ electrons of the twin {Sc, Cr}. There is a useful notion to discuss of the interactions, we will call equatorial position. In a general way the orbiting planes de of the couples of twin electrons intersect along straight lines having between two successive straight lines the highest possible angle. That is 90° for two couples, 60° for three couples and so on. Similarly, between two twin electrons the difference of angular position on their respective trajectory is of 180° , that between twin couples share this angle according to the number of couples in the subshell.

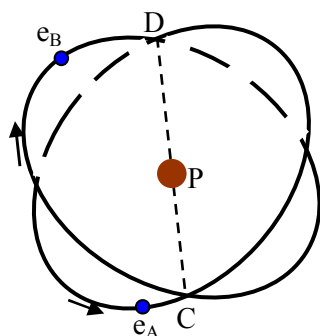


Figure 3. The orbiting plane of two electrons having equal and opposed magnetic momentums.

3.1 The kernel of the atom and its outer electrons.

Call ns and np the electrons of the outermost electronic shell of the rare gases preceding the considered element and $(n + 1)s$ and $(n + 1)p$ the outermost electrons. The interpretation of the crystal structures of metals point out that during the filling of the different electronic shells in a row of elements of the periodic table, the outermost electrons $(n + 1)s$ and $(n + 1)p$ play a different role from the already present electrons on the rare gas preceding the considered element. The different role comes from their different extension and period. In particular for the metals having none $(n + 1)p$ electrons, the one or the two $(n + 1)s$ electrons develop less bonds than the eight ns and np electrons. These last develop bonds with the nearest neighbours; as for the $(n + 1)s$, they are pushed away in direction less obstructed, as a result they enter in bond with second neighbours. On the other hand with different period the possibility of synchronous bonds (see section 4) is reduced increasing the disorder in the orientation of the atom in respect of their neighbours. For this reason we will call kernel of the atom the nucleus and the electronic shells with a principal quantum number lower to that of the $(n + 1)s$ and $(n + 1)p$ outermost shells.

3.2 Windows upon the nucleus, covalence, ionicity and overlapping bonds.

The np , nd and $4f$ electronic shells of the kernel of the atom allow to see in different way the $(n-1)$ shell through a zone that we will call window² (n here refer the outermost shell of the kernel of the atom or a deeper shell). For the understanding of the crystal structures it is useful to characterize these differences. Indeed, it is through these windows that the neighbour atoms are attracted and built the considered site. For the np shells as a result of the small number electrons the windows are wide, allowing different sites: the most commons be-

² We just consider the fourteen elements going from lanthanum to ytterbium called $4f$, we leave to spetialists of the fourteen elements following the radium called $5f$, to extend this study.

ing the tetrahedral and octahedral sites. As the np outer shells of the kernel of the atom are closed they play an important role in the interaction between atoms.

At the beginning of the filling of the nd or $4f$ shells, the windows through the np shell are just a little modify and allow seeing the additional charge of the nucleus. Afterwards during the filling of the nd or $4f$ shells, the intra-atomic distribution of the electrons of the first subshell exhibits, simplifying a little, a conical window centred on the equatorial plane which, in the concerned directions between the AC and BD circle on the Figure 4, leaves the nucleus with a lower screening constant than in the other directions, we will call it equatorial window. This distribution exhibits equally a second window in the both directions of the Pz straight line; we will call it polar window. On the other hand the electronic distribution of an atom has a heteropolar structure which favours the overlapping bonds between the high electronic density and the windows toward the nucleus. With heteropolar structure one has to understand that the electrons with their movement define planes of strong electronic density and in these planes for the elliptical trajectory along the major axis of the ellipse a direction of strong electronic density. As a result between these planes and these directions there are hollows or windows on the nucleus, which we will call secondary, attracting an electron in its direction of lowest electronic density. It is this interatomic overlapping which gives the more or less strong covalence according to the atoms and the site in the molecule or the crystal.

The nd or nf equatorial window fully appears as soon as the first subshell is fill up. It remains and the intensity of its capacity of attraction varies during the filling of the second subshell. The capacity of attraction of the polar windows equally varies in intensity, its angle of opening decreases when the second subshell finishes filling. Numerous consequences of valence that is of bonds result of them. Let us first notice the new shed light brought on the complexes of coordination. Through these windows it is a positive charge which is visible; from this fact the atoms with a great number of electrons as the metalloids are easily attracted. One has to see there an important element in the choice of the octahedral site by the atoms of numerous metallic compounds or in the formation of the octahedral complexes for example in the ferrocyanurs of $K_4Fe(CN)_6$ type. Similarly the octahedral site of numerous compounds, in particular of the $3d$ metals, is built by the capacity of the metal to have the octahedral coordinance. When the number of the $3d$ electrons increases, the angular opening of the polar window decreases; the octahedral coordinance has a tendency to give way to the square planar coordinance exhibited with several compounds or complexes of copper.

The discovery of the rare gas compounds establishes that the chemical bond at least in these compounds is not governed by the transfers of electrons. An atom as that of the fluorine is attracted by the xenon. One has to understand this ability as the result of the interaction of two different atoms each one having windows on the positive nucleus and direction of electronic movement allowing overlapping bonds, each atom being positive and negative according to the considered direction. It is the covalent bond.

For the $3d$ shell, the copper well exhibits, in the high Tc superconductors as $YBa_2Cu_3O_7$, an equatorial window with its square planar coordination. Now for the polar window in all the Cu, Tl and Hg based superconductors the apical oxygen corresponding to this window exhibit's a more important distance than the classical one [5].

Consider now the bond called ionic. With neutral atoms one has to consider as more or less covalent all bonds. A bond will be strongly covalent if the interaction: electron-window on the nucleus is strong; it will be ionic in the opposite case. A first indication of this approach concerns the metal-metalloid distances. For example in a crystal an atom of metal will

be all the more ionic that the volume of the crystallographic site is large, from this angle the alkaline monochalcogenides can be range as more ionic than the alkaline earth oxides and so on [4].

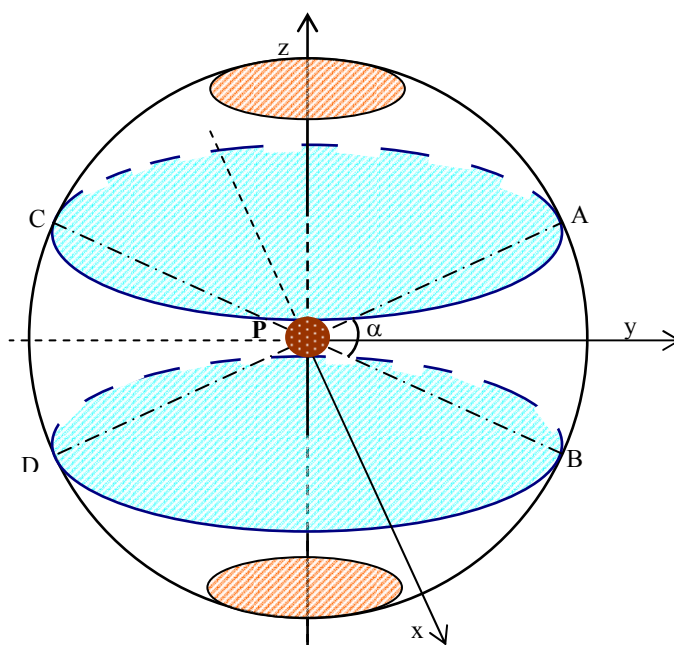


Figure 4. Windows on the nucleus. The equatorial window centred on the corresponding plane is delimited by the AC and BD circles in blue green on the figure. The polar window centred on the Pz axis, shown by small circles on the figure.

Now the more or less covalent or ionic character of a bond is not specific of the cations; a same anion can exhibit different intensity of its covalent character. In this view the La_2O_3 structure brings an important element: the oxygen of the octahedral site is more ionic than that of the tetrahedral site that is corroborated by the distances, the shortest distances corresponding to the strongest covalent bonds [4]. Furthermore the oxygen of the octahedral site is rather easily substituted by sulfur, selenium or tellurium showing the lower covalence than that of the other chalcogenides. One can see there the role of the eccentricity of the trajectory of the outermost $(n+1)s$ and $(n+1)p$ electrons increasing when going from oxygen to tellurium.

4 The synchronous bond

There is in the solids a mechanism of order-disorder which is an important clue to understand the crystal structures. For simplicity consider first a crystallized solid. In its crystallographic site the atom takes an ordered position to low temperature correlated to the synchronous motion of the outer electrons between neighbour atoms. We will say that the atom has with its neighbours synchronous bonds which are directional. When the temperature increase the atoms are supposed vibrate in their site.

4.1 The synchronization of the electronic motions.

To characterize synchronization consider in a crystal a chain of atoms of the same chemical species and the same crystallographic site. Furthermore consider two neighbour atoms and on each one of them an electron in the same quantum state. To simplify the figures we suppose closed and periodic their motion but the following reasoning are still the same with al-

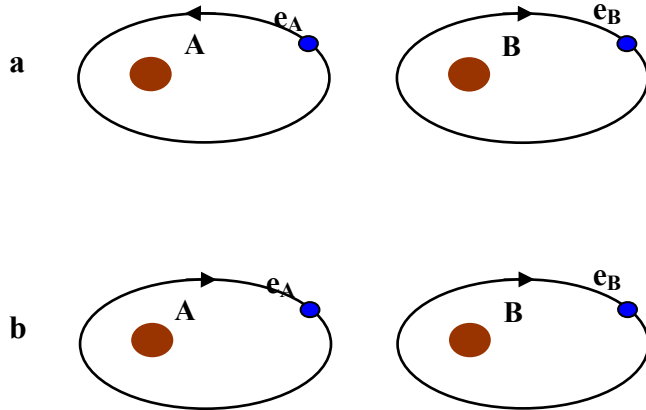


Figure 5. The synchronous movement: a) antiferromagnetic coupling, b) ferromagnetic coupling

most closed motion. For each one of these electrons the period of the associated motion is thus the same one. May be in this chain A and B two neighbour atoms and on each one of them e_A and e_B the electron considered (Figure 5).

There are two cases of figure to consider in respect of a reference plane, depending on the two electrons turn either in opposite way (Figure 5 a) antiferromagnetic coupling or in the same way (Figure 5 b) ferromagnetic coupling.

Without disorder at zero degree Kelvin there is correlation between the motions of the conduction electrons in such a way to have the maximum cohesive energy. For example the electron e_A comes between A and B when e_B is as far as possible from e_A . The cohesive energy of the electron e_A with the atom B is thus at its maximum value. The kernel of the atom B thus attracts the electron e_A but the presence of e_B prevents it to leave its atom. In a similar way for e_B with its other neighbours in the same chain and so on.

Thus each binding electron is attracted more by the kernel of its own atom than by that of a neighbour. It is the same for all the directions where there are identical chains. There is synchronisation of the motion of the electrons in the same quantum state on an atom of the same chemical species located in the same crystallographic site. This notion of synchronisation is still valid, step by step in successive neighbours, in noncrystalline solids.

4.2 Synchronization, transfer of thermal energy and disorder

Consider then the solid at sufficiently low temperature so that absorbed energy preserves synchronization between the greatest number of homologous electrons. Synchronization has a role in the transfer of the energy. Indeed, at the time of the interaction of a gas atom with the wall of the solid, a part of energy of translation of the atom of gas is transferred on one or more electrons of one or more atoms of the solid. Consider an electron e_A which has absorbed this energy. The binding energy E_ℓ to its atom varies. Synchronization with its neighbours is not respected any more. The electron e_A tends after a certain number of revolutions to pass between the atoms A and B at the same time than e_B . This tendency causes to modify the period of the electron e_B by transfer of energy. Step by step the electrons homologous with a same site tend to preserve synchronization. This is shown by the study of the heat capacity of the solids at low temperature [11]. So that the tendency to preserve synchronization takes place, it

is necessary however that transferred average energy for one direction remains weak compared to E_c energy of bond to its atom. There are such bonds with all the outermost electrons in the different directions of the space, a priori the corresponding energy being not the same. Then consider an atom, when the thermal energy is higher than a gap E_g lower than E_c , we suppose that the synchronous bonds are broken and that the atom tips out in a disordered state.

4.3 *Synchronization and chemical disorder*

Underline that the synchronization is a hypothesis reinforced by the recent interpretation of Dirac's theory based on the trajectory of the electron [3]. Several experimental results corroborate it: among them the lowering of the order-disorder temperature with the introduction of impurities as the melting temperature of metals with a small amount of another metal. In comparison of the analogous electrons to those of the main metal, those of the impurity have different periods and the synchronization disappears leading to a lower cohesion and the lowering of the order-disorder temperature in this case the melting temperature. We recognize there Raoult's law well known of the chemists [12].

4.4 *The limits of the notion of ionicity.*

The periodic motion of the electrons allows shedding light on the notion of ionicity. The laws of the mechanics teach us that speed of the electron decreases when it moves away from the nucleus. As a result when there are few outer electrons as the ns electrons of metals, these being attracted in the positive direction resulting of the presence of the neighbour atoms, they spend more time in the vicinity of this neighbour than on their own atom, but the fact to turn around the nucleus of this last allows to say that they belong to their atom. Consequently the study of the electronic density to put in view the ionic character of a crystal can easily one to believe to the validity of the ionic hypothesis, since hiding the periodic motion need to understand the atom and its interactions.

On the other hand, notice that the metallic character of the monochalcogenides of the rare earths is easy to understand with the synchronous bond as for numerous metallic compounds or superconductors.

5 **The crystal and the atom**

If the crystals clearly exhibit anisotropic properties, nevertheless the interpretation of their crystal structures has been largely led by the spherical approach of the atom. Kittel in his book "Introduction to Solid State Physics" summarizes well this fact in the chapter on the subject [13]. Wyckoff in his encyclopaedia "Crystal Structure" gives the substantial developments on the interpretation of the crystals from the spherical approximation of the atoms or of the ions [14]. Among the positive aspects of this approach we can underline the simple understanding of the faced cubic close-packing (fcc) and of the hexagonal closed-packing (hcp) observed for numerous metals. Furthermore notice that the (fcc) structure is equally that of the rare gases in the solid state. These two structures corresponding to the closest packing between identical spheres there is a convincing interpretation for an approach where the atom is considered as a sphere.

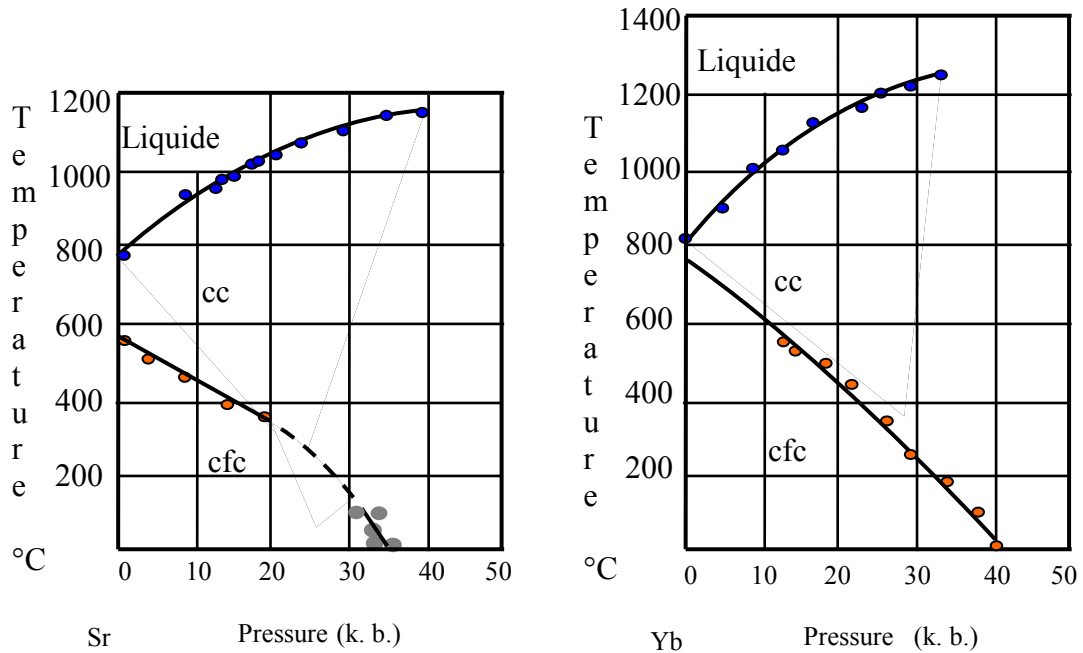


Figure 6. The phase diagram pressure-temperature of strontium and of ytterbium [15][16].

However there are several difficulties to restrict the interpretation of these two structures to a packing of spheres. To be more convincing the model would explain how the metal choice between the two fcc or hcp structures. Furthermore there is an experimental result which contradicts this model. The metals strontium and ytterbium crystallize at the atmospheric pressure with the fcc structure and exhibit the body centred cubic bcc structure, theoretically less compact, under pressure of the order of 40 to 50 Kilo bars to room temperature [15], [16], Figure 6. The difficulty comes from that the solid state cannot exist without directional bonds. This approach is in fact underlying in the works of Torben Bergman in 1773 and René Just Haüy in 1782 who suppose the existence of elementary blocks [17]. From experimental results, it is important to underline that helium is the alone liquid element to atmospheric pressure and all temperature, it is also the alone one with just circular electronic trajectories [18]. In fact the atoms are essentially dissymmetric, as a result to understand crystal structures it is, among numerous aspects, to understand how despite their dissymmetry atoms can, in a large number of cases, be likening to spheres.

5.1 Disorder and crystal symmetry

We know that several properties of crystals are in connection with the presence of impurities as the semiconductor character or the colour of different gemstone jewellery: the blue of the cobalt in sapphire, the red of the chrome in the ruby to just quote these two crystals. In these cases although the presence of impurities the crystal keeps its structure. On the other hand apart from impurities there are different possible defaults as dislocations, stacking fault for example. The study of fcc and hcp structure leads to put in view a fault of periodicity not yet discussed in its understanding and that we have now to tackle.

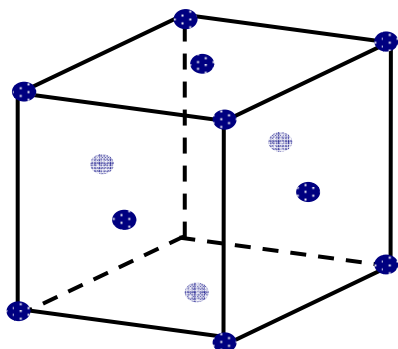


Figure 7. The fcc structure

The crystal structures are determined from their X-ray, electrons or neutrons diffraction patterns. The interpretation of these patterns uses the symmetry of the point groups where the atomic positions are considered as points. From this point of view the atomic dissymmetry is ignored. But from a strict geometrical approach with dissymmetric atoms, it is useful to underline that the cube would not be exhibited as a crystal structure. Indeed in a cube there are four body diagonals which link two by two, two opposite apexes. Yet there is no strictly periodic lattice built with non spherical objects able to make identical the four diagonal of a hexahedra. If we search to build an arrangement with three equivalent directions; in a first step we will put together the atoms in planes since we will stack up them, thus we can build three diagonals of the cube but the fourth has its properties determined by those of the three others. For example it will be the easy direction of magnetization in some cubic magnetic compounds, a difficult difference to detect on a non magnetic aspect. Nevertheless if we still observe cubic structures this comes from a small disorder, which is sufficient to maintain the cubic structure, the atomic dissymmetry being too small to generate a corresponding structure. From experiments the disorder is revealed in the mosaic structure of the crystals; Guinier thus conclude a discussion on the crystal perfection "In the majority of the cases, the ideally imperfect crystal is a better approximation than the perfect crystal" [19].

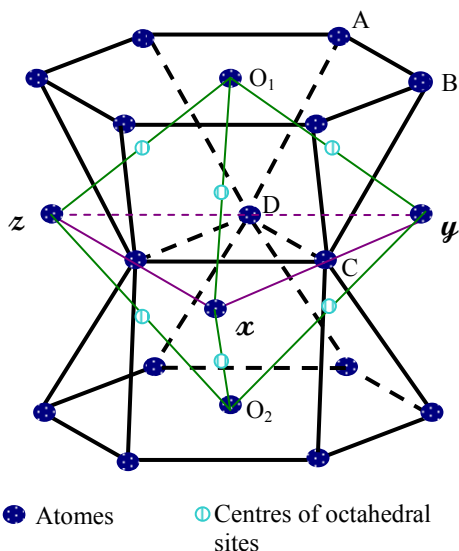


Figure 8. Hexagonal close-packing

In fact the atomic symmetry is always lower than that of the sphere and it is almost always a higher symmetry than that of the atom which is observed in the crystal. It is for example the interactions resulting from the equatorial and azimuthal window which built the space without further bonds coming from the synchronous bonds at the kernel level. The study of the hexagonal close-packing, Figure 8, allows putting in view this structural aspect. The two atoms in O_1 and O_2 are equivalent. The straight lines linking three of the centres of the neighbour octahedral sites for each of these atoms make a system of orthogonal axes. But one can see that the system associated to O_1 and that to O_2 as presented on the figure are different. Thus there is a dissymmetry on each side of the compact plane to which belongs the atom and each atom can choose its orientation in one of this two systems.

Yet, for the elements crystallising with the hcp structure, nothing in the diffraction diagram reveals the existence of this two systems of axes. We have to conclude that the disorder hides this aspect of the hcp structure. Nevertheless there is a structure describe as a double hexagonal packing, in which some metals as lanthanum crystallize, where these two systems of axes allow its interpretation. The classical interpretation of this structure supposes the

ABACABA... packing of the three types of A, B, C compact planes; as a result in one plane from two the atoms are in an hcp or fcc neighbouring. Considered alone, all the atoms are identical, we so suppose that they must occupy an identical crystallographic site and we do not retain this structure for lanthanum [20]. To make identical all the atomic sites we just need to suppose that in one plane out of two the atoms take the ones towards the others a defined orientation in one of the systems of axes and the same in following plane but in the other system of axes. In the succession of the compact planes this leads to distinguish the $A_1 B_1$ and $A_2 B_2$ planes, the stacking to be considered is then $A_1 B_1 A_2 B_2 A_1$.

5.2 *The crystal and the valence*

During the nineteenth century it became apparent that in a defined compound, there is a relatively specific rule between the proportions of the different constituent elements. This rule is known under the name of valence can be expressed as "The capacity of combination or substitution of an element with or to the hydrogen". The interpretation of the notion of valence and that of ion have led to the octet rule: the atoms tend to lost or to gain electrons in such a way that their outermost shell has the configuration of that of a rare gas which was for a long time supposed inert. The rule of the octet comes from that that it is either the number of missing electron in comparison of the rare gas following the element, or the number of additional electrons after the rare gas able to determine the valence. However in the crystal state the understanding of the valence need to take into account the existence of bonds exhibited with the contraction of the volume as in the study of the monochalcogenides [4]. This property is found again for the first elements of the periodic table in different lines. For these metals, the study of the crystals and of their corresponding volume put equally in view bonds which are the signature of the additional charge after the rare gas preceding them Figure 9. The numerical data have been taken from [21] [22].

This variation of the atomic volume of the metals shows equally a parallel with the valence. The alkaline metals are monovalent and lead to compounds of ionic type. This property is interpreted attributing this valence to the $(n + 1)s$ electron where n is the number of the outermost shell of the rare gas preceding it. With a good approximation the kernel of the atom is equivalent to a positive charge keeping this electron. This one orbits relatively far away from the kernel of the atom as it is shown by the large increase of the atomic volume in comparison to that of the preceding rare gas. However it leaves the kernel of the atom with an attractive charge of the order of the unit in a great number of directions leading to bonds between: electron of valence and kernel of neighbours.

With two $(n + 1)s$ electrons one observes a large contraction of the atomic volume. The charge of the kernel of the atom is of the order of two and active in a great number of directions. So the contraction of the volume is to be attributed to the increase of the charge of the kernel allowing, in the crystal state, bonds between: the two electrons of valence of an atom and the kernels of two other neighbour atoms. Thence there is a parallel with the valence two of the alkaline earth metals and their atomic volumes compared to that of the alkaline metals. On the other hand these elements crystallize in the hc, cfc or bcc structure without any possibility to associate a characteristic volume of the structure.

With two $(n + 1)s$ electrons but in addition a third electron on the $(n + 1)p$ or nd or also $4f$ for lanthanum shell a further contraction is observed but still no more characteristic influence of the crystal structure which is hexagonal for one of those of the bore, fcc for aluminium, hcp for scandium and yttrium and double hcp for lanthanum. In "Crystal Structures and Bonds"

we had already observe the small influence of the structure on the molecular volume of the $3d$ monochalcogenides, this means that the difference between two structures is first the direction of the possible bonds. The third nd electron orbits in the neighbours of the surface of the kernel of the atom; from outside the kernel the additional charge of the nucleus is still visible in most of the directions. There is still reason to attribute the contraction of the atomic volume to the increase of the charge of the kernel.

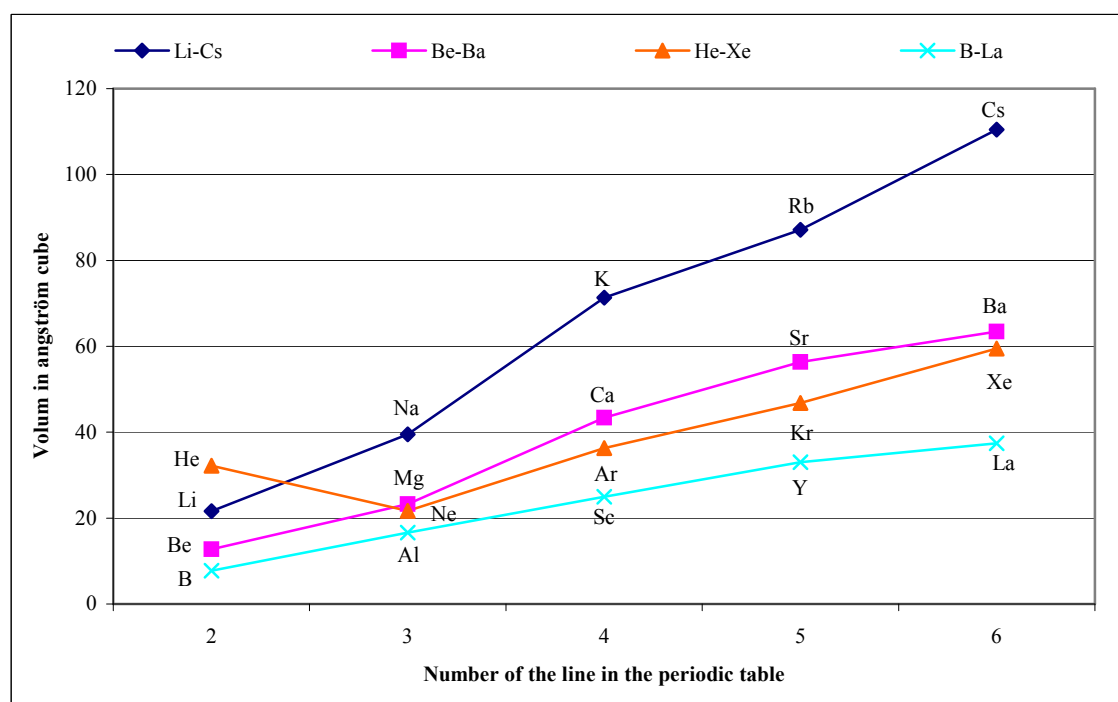


Figure 9. The volume in \AA^3 of the firsts, seconds and thirds elements, from the second to the sixth line of the periodic table, comparés à celui du gaz rare qui les précède.

Thus there is still a parallel between the valence three of these metals and their atomic volume. The deep position of the $4f$ electron in the kernel of the atom requires understanding the mechanism of bond. The two $6s$ electrons are attracted by the kernel of one or several neighbours. This attraction is reinforced with the strong eccentricity of the $6s$ electrons. Concerning the third charge of the nucleus of the atom, it is neutralized by the $4f$ electron except in the directions of the polar or equatorial windows being stabilized by synchronisation on a same crystal site. On the other hand for the other $4f$ electrons, they are equally deep and orbit in directions of plane apart that of the equatorial one. As a result their number and their deepness do not allow window on the nucleus. Thus the kernel of the atom is without additional power of attraction and the first $4f$ electron is often the alone to contribute to bonds thanks to the apparent charge of the kernel of the atom.

Thus there is a parallel between the atomic volume of the metals and their valence as between the molecular volume of the monochalcogenides and the valence of the corresponding metals. However with a model of neutral atoms in ionic compounds as in the others the understanding of the valence in crystals needs a new light. We know that the xenon rare gas, the most studied gives numerous compounds [21], [23], [24]. This property leads to suppose that

the xenon shell in the rare earth elements and the barium or that of the krypton in the strontium play a role of valence [25], [26]. By role of valence one has to understand a role of bond, the np or ns electrons of an atom being able to be attracted by the positive kernel of a neighbour atom. By analogy this role of bonds of the xenon or krypton shell suggests that it

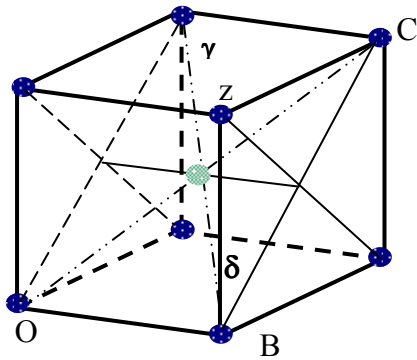


Figure10. The bcc structure

must be the same for $3p,s$ shell with the $3d$ elements, $4p,s$ with the $4d$ elements and so on. This contribution of valence of the nps shell of an atom of metal for a metalloid as the oxygen can be of one or two units according to the site of each considered atoms. The study of the spinel structure will bring an example of such a possibility.

When the nd or nf shell tends to be full, the large number of electrons of the shell tends to fully screen the additional charge of the nucleus except eventually in the direction of the equatorial window, as confirmed by the valence III of ytterbium.

6 Crystal Structures and Bonds

The experimental facts that constitute our knowledge of the crystal state refer to the space notion. The space do not exist by itself, it is the substances which constitute it. This is true for the molecules and also for the crystals which are in a given extend molecules of infinite dimensions. But the atoms cannot combine in any proportions. Indeed the neighbours of an atom cannot take any positions around this atom. Their respective properties require rules of neighbours. Thus the organization of the atoms in a crystal must result of the properties of the atoms but not of those of the defined space according to the periodicity of the arrangement of the atoms. The periodic properties observed in the crystals are the result of the possible bonds between the involved atoms. It is this approach which was at the root of the interpretation of the La_2O_3 [4]. It equally emerges in the study of the superconducting copper-based compounds where the square planar coordination of copper plays an important role [5]. We have seen it in 3.2, this coordination of the copper reflects the property the $3d$ equatorial window; similarly the valence three of the rare earths discussed in 5.2 reflects the property of the $4f$ equatorial window. These results among others characterize the atom as well the quantum state, leading to speak of equatorial plane of the atom even if in fact the equatorial plane is a quantum property of the electrons of a given shell.

Thus to understand the building of the crystal space, it is to perceive the shape and the properties of the atoms and understand their organization. From this angle; now search what is leading the atoms to build the crystal structures fcc, bcc and hcp. The volume being not the important characteristic one has to consider the orientation of the atomic space considering that of the structure. This orientation is determined by the possible bonds with regard to the neighbour atoms. In a first approximation, the atomic space can be described as its kernel relatively spherical with one or two $(n+1)s$ electrons orbiting around more or less far away. This dissymmetry of the atom is an important clue to understand the crystal.

6.1 The body centred cubic structure.

Numerous metals crystallize with the bcc structure. The classical interpretation for the alkaline metals supposes that the large spherical volume of the atom impose a smaller number

of neighbours than in the fcc structure of the rare gases. For these metals the increase of the volume in comparison with the rare gas preceding each of them, comes from the large orbiting distance between the $(n+1)s$ electron and the kernel of the atom. Indeed, the screening factor of the nucleus for the $(n+1)s$ level is more important than that of the ns or np states; as a result the electrons of the ns or np shell see a charge of about eight to nine units higher to that of about one unit seen by the $(n+1)s$ electron of the alkaline metals (see appendix). As a result the size area of the $(n+1)s$ electron considering the kernel of the atom is more important than the alone influence of the eccentricity, so the large increase of the atomic volume.

This difference of size area leads the atoms to expand bonds giving to the $(n+1)s$ outermost electron a larger place than that devolved to the kernel of the atom. In other words crystal packing respects this aspect of the atomic dissymmetry. This result is obtained if the $(n+1)s$ electrons extend their trajectory in direction of their second neighbours, like this they play a role of cement between the kernels of the nearest neighbour atoms.

For each alkaline earth we suppose that the diameter of extend of the kernel of the atom is practically the same than that of the rare gas preceding it. The rare gases crystallize with the structure fcc allowing to compare the two structures. The body diagonal of a cube is equal to $a\sqrt{3} \approx 1,732a$ if a is the lattice constant; the face diagonal is $a\sqrt{2} \approx 1,414a$. Then compare the interatomic distances of neon crystallising fcc and of sodium crystallising bcc. Their ratio is 0,843. Suppose the kernels of atoms in contact with a diameter close to that of the rare gas preceding the alkaline metal. Compare the distance $0,843a(\text{Na})$ to the two diagonals, it comes:

$$a(\text{Na})\sqrt{2} < 2 \times 0,843a(\text{Na}) = 1,686a(\text{Na}) < a(\text{Na})\sqrt{3} \quad (6.1)$$

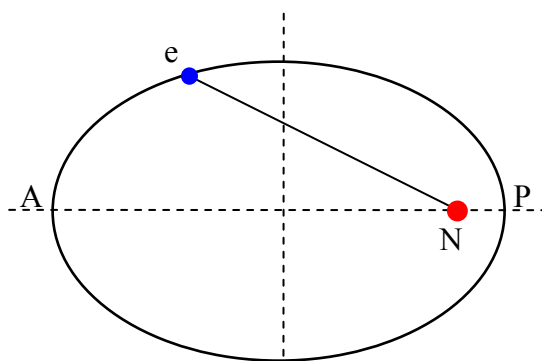


Figure 11. Elliptic orbit. In N the nucleus and in e the electron. In A the aphelion of the trajectory.

It is the same for all other alkaline earths going from Na to Cs as compared to the other rare gases preceding them. For Li compared to He the respective charges being weak it is the lithium which has a weaker volume than He, but the volume of Li equally varies very largely, the charge of the nucleus going from two to three. We then suppose that the conclusions for the others alkaline are still valid for Li.

This comparison allows saying that the interactions developed by the electron $(n+1)s$ are not sufficient to keep the fcc structure of the rare gases. For further developments it is

needed, if possible, to determine the orientation of the equatorial plane of the considered atom in comparison of the crystal space. Thus determining this orientation in different structures we will be more able to understand their difference and that which allows a phase transformation.

This orientation is determined by the interactions which the near neighbours. They are developed in the direction of the windows open toward the nucleus attracting the np and ns electrons of the neighbour atoms with a charge of about the unit. The angle of the plane of the motion of the ns electrons with the equatorial plane being the same for all the n level, the trajectories of the ns electrons are equally directed toward second neighbour but different from that of the $(n+1)$ electron.

The apparent charge between the kernels of the neighbour atoms being weak for the alkaline metals one has to suppose that the attraction is developed mostly between the equatorial or polar windows and an electron from the kernel of a neighbour this for the greatest number of possible neighbours. In the bcc structure the δ angle between one of the directions of the height nearest neighbours, that is the body diagonal and a diagonal of a face of the cube is 35° ,²⁶ Figure10. It is close of the angle of 30° for two np electrons with the equatorial plane. As a result a stable orientation of the equatorial plane of an atom is perpendicular to one diagonal of a face of the cube. On the other hand with this orientation the $(n+1)s$ electron and the two ns electrons can develop bonds with their second neighbours along an edge of the cube. Thus tackled the body cubic centred structure of alkaline metals finds a beginning of understanding by comparison with the faced centred cubic structure of the rare gases which remains to be understood.

6.2 The faced-centered cubic structure

According to their electronic configuration the elements crystallizing with the fcc structure can be divided into two groups: the elements of the rare gases and the others. For the first their electrons built the shells ns^2, np^6 . For the others they always have the ns^2, np^6 shells fill up and the $(n+1)s$ shell with most often two electrons. On the other hand the lithium with the $2s^1, 1s^2$ configuration exhibits to 78°K the fcc structure [14].

The fcc structure of the rare gases

For the elements of the rare gases their temperature of solidification is weak as compared to that of the alkaline metals, the bonds taking place with the different electrons are then weak. The difference of eccentricity between the ns and np electrons and the higher number of np electrons, impose an arrangement allowing to the electrons ns , having the largest eccentricity, to orbit in a direction giving to them a sufficient place. The (6.2) relation gives the eccentricity as function of the n and ℓ quantum numbers, the Table 4 gives their values with the corresponding elements. It increases with n as well as the melting point. The increasing eccentricity leads to the overlapping of the trajectories between neighbours atoms and then the stability of the structure. This fact leads to suppose that the increase of the melting point is correlated to that of the eccentricity.

$$\varepsilon_{n\ell} = \left(1 - \frac{(\ell+1)^2}{n^2} \right)^{\frac{1}{2}} \quad (6.2)$$

Table 4. The eccentricity of the different s, p, d and f electronic trajectories électroniques according to their shell .

He, Li, Be		Ne, Na, Mg, Al			A, K, Ca, Sc		Kr, Rb, Sr, Y			Xe, Cs, Ba, La		
1s	2s	2p	3s	3p	4s	3d	4p	5s	4d	5p	6s	4f
0	0,866	0	0,943	0,745	0,968	0	0,866	0,980	0,661	0,917	0,986	0

See now in which extend the respective dimensions a of the semimajor axis and b of the semiminor axis of the ns and np trajectories allow the fcc structure. Their ratio is given by the relation [2] :

$$\frac{b}{a} = \frac{\ell + 1}{n} \tag{6.3}$$

Call $\delta_s = NA$ the distance of occupancy of the ns electrons ns Figure 11. It comes:

$$\delta_s = a(1 + \varepsilon) \tag{6.4}$$

Consider $\rho_b = \frac{\delta_s}{b}$ the ratio of occupancy. It comes:

$$\rho_b = \frac{n(1 + \varepsilon)}{(\ell + 1)} \tag{6.5}$$

For $n > 1$ this ratio is always higher to $\sqrt{2}$. If the semiminor axis is in a direction close of one or several nearest neighbours the occupancy of the trajectory is compatible with the compact fcc structure. The major axis will be oriented in such a way that the trajectory of the involved electron can be expended in a direction close to that of second neighbour. With these considerations there are still an important number of orientations of the orbiting plane which as a result more or less fluctuate.

In the fcc structure the two atoms of an edge (Figure 7) set at the apexes of the cube are each one a second neighbour of the other, those of the centre of a faces are their nearest neighbours. Consider the α angle between the motion and equatorial planes. There are four trajectories with $\alpha = 60^\circ$ and two with $\alpha = 30^\circ$. Suppose that the equatorial plane of an atom

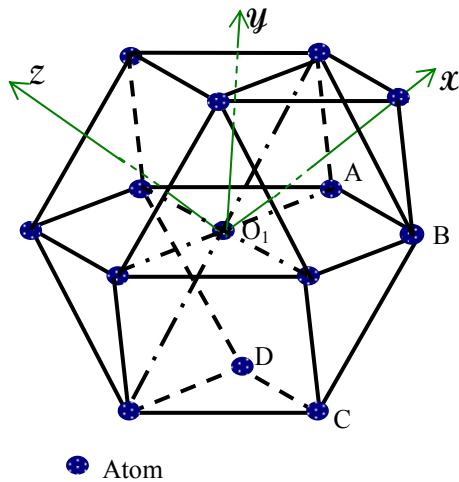


Figure 12. The close-packing in the fcc structure.

is close of a face of the cube; according to the disorder resulting of the lake of synchronization between the ns and np state, the np orbital with $\alpha = 60^\circ$ can find a direction near of that a nearest neighbour having its equatorial window in the corresponding direction. The body diagonal makes an angle of $54,74^\circ$ with an edge Figure 10; if the major axis of the trajectory of an electron np takes this orientation it is oriented toward three nearest neighbours. Furthermore if the equatorial plane is perpendicular to one of the face of the cube, the four np electrons can take the same property. Point out that thus the atom with four np electrons develops bonds with its twelve nearest neighbours (Figure 12). On the other hand the aphelion of the ns trajectories can then be oriented toward the nearest neighbours. We suppose that there are such bonds which allow to the atom of rare gas to stabilize the fcc structure.

The fcc structure of Ca and Sr

The metals of the beryllium column have volume close to those of the rare gases preceding them Figure 9. The analysis which has just been mad for the rare gases is still valuable for the fcc structure of the Sr and Ca. The expand of each of the two $(n+1)s$ trajectories in comparison to the kernel of the atom with a visible charge of the order of two is lower than for the

alkaline metals. Furthermore the bonds with the neighbours are stronger as a result of the two additional charges on the nucleus as confirmed by the increase of the melting point.

6.3 *The cfc → cc transformation.*

The phase change from bcc to fcc between alkaline and alkaline earth metals is linked to the double number of the $(n+1)s$ bonds and to the shrinkage of the atomic volume resulting of the increase of the charge of the nucleus giving to that of the kernel seen by the $(n+1)s$ electrons a charge of about the double.

To understand the fcc → bcc phase change observed under pressure with Sr one has to point out two aspects favouring it: on one side it seems natural to suppose that the increasing eccentricity of the $(n+1)s$ and np trajectories plays an important role, on the other side it equally matter to notice that for strontium and ytterbium the equatorial window open on the nucleus with respectively ten or fourteen additional charges less screened than in the other directions. These two aspects favour bonds between second neighbours which are thus able to dominate. On the other hand the number of neighbours changes, this fact leads to suppose a change of the orientation of the equatorial planes which take that suggested for the bcc structure of the alkaline metals. In the both structures each $(n+1)s$ electron, as a result of the eccentricity of the trajectory, orbits toward a second neighbour when it moves away from the kernel of its atom.

The pressure moves closer the atoms; the strength of the bonds between second neighbours' increases but the kernel of the atoms with an important number of electrons cannot be contracted. Then it appears under pressure repulsive interaction as much stronger than the eccentricity is stronger: in particular in the fcc structure the bonds between the np electrons and the nearest neighbours along the body diagonal of the cube. On the other hand the change of orientation of the space of the atom with respect to that of the neighbours allows a better overlapping of the bonds stabilising the bcc structure. It seems reasonable to understand in this way the change of structure.

Consider now the barium, it crystallize in the bcc structure [21] [22]. The barium comes after the strontium in the periodic table. The eccentricity of the trajectories is more accented for all the ns , np and $(n+1)s$ electrons with $n = 5$. The result is to give stronger bonds, which are equivalent to the effect of the pressure.

Consider now the ytterbium which crystallizes with the fcc structure. This element has its 4f shell fill up with fourteen electrons. Its atomic volume in the fcc structure is lightly smaller than that of the fcc calcium that is: $V(\text{Ca}) = 43,34\text{\AA}^3$ and $V(\text{Yb}) = 41,28\text{\AA}^3$. The difference with respect to calcium comes from the ns , np and $(n+1)s$ electrons with $n = 5$ which are the same as those of the barium. The difference with respect to the barium comes from contraction of the kernel resulting of the fourteen additional 4f electrons. These remarks show for this element its similarity according to the crystalline properties with Ca and Ba, allowing understanding its fcc → bcc phase transformation under pressure.

6.4 *The CICs and ClNa structures*

With neutral atoms the compounds called ionic match to a set of atoms having an occupancy sometime near by if not relatively close or inverse with respect to the occupancy of the ions [5]. On the other hand the CICs structure is interesting considering the neutrality since numerous inter-metallic compounds crystallize with this structure and corroborate by this way the hypothesis of neutrality.

Consider the bcc structure; it can be describe as a double simple cubic lattice. Underline that even with neutral atoms the ion notion keeps value; indeed the atom of caesium remains in numerous directions a positive charge close to the unit, as for the chlorine atom with seven $(n + 1)$ electrons on the s and p shells it is negative in numerous directions and thus attracted by the caesium. Let us suppose then for the caesium the same orientation of the equatorial plane than for the bcc structure, Figure 10. The trajectories $(n+1)s$ of the atoms of caesium have a large eccentricity, along an edge of the cube the corresponding electrons can thus have synchronous bonds between them. On the other hand for the kernels of the atoms in position of nearest neighbours they are of different chemical species they cannot make synchronous bonds. As a result it is the columbic attraction with the windows on the nucleus which attract the kernels between them whatever their chemical nature be. Consider now the chlorine atoms, one has to suppose the same orientation of their equatorial plane as for the structure bcc. The eccentricity of the $(n+1)s$ trajectories his smaller than those of the caesium atoms, the corresponding bonds are less cohesive. Thus the ClCs structure has similitudes with the bcc structure. The $(n+1)s$ nature of the conduction electrons in the high T_c superconductors corroborates this approach [27]. Indeed the crystal structure of these compounds has similitudes with that of the perovskite which itself has similitude with that of ClCs.

Considering the ClNa structure it is as for ClCs a double lattice of each chemical species. The sodium atoms occupy the octahedral site of the fcc lattice of the chlorine atoms and reciprocally. Consider the ClNa \rightarrow ClCs phase transformation under pressure exhibited by the alkaline halogenides [28]-[33] and the inverse transformation when the temperature increases [22]. If we suppose for the metallic lattice the same arrangement as for the pure metal, the transformation can be interpreted as for the cfc \rightarrow cc transformation under pressure of Sr and Yb. For the metalloid the equatorial planes can be parallel to those of the metal. The respective angular orientation of the kernels of the two species is determined by the trajectories np ; with respect to the lattice crystal they must be different in such a way to allow the strongest cohesion.

6.5 *The hexagonal close-packing structure.*

Numerous metals crystallize with the hcp structure. The difference with respect to the fcc structure must be attributed to the axial dissymmetry of the kernel of the atom. Several experimental results allow corroborating this approach.

The table 5 recalls the structures of some metals. The first interesting result concerns the way going from the fcc structure with calcium to hcp structures with scandium and the same for strontium and yttrium. It corresponds to the occupancy of the first $3d$ or $4d$ state.

This occupancy corresponds to an additional charge on the nucleus which can interact with the nd electrons of the neighbour atoms through the equatorial or azimuthal windows, reinforced interactions by their synchronization. Indeed the additional charge is not screened by the electrons of the kernel of the atom. This change is also observed with the rare earths going from Ba to La with the first $4f$ electron, then between Yb and Lu. The increase of the charge of the nucleus is equivalent to a high pressure. This leads to discuss the way going from the bcc Sr or Yb type structure under pressure to the hcp structure. In this structure we have chosen the body diagonal as straight line perpendicular to the equatorial plane. The increase of the charge visible through the windows allows considering it as responsible of the way going to twelve neighbours still keeping the same orientation of the equatorial plane. But the high

dissymmetry generate by the additional charge at the nd level and visible through the windows reduce the disorder of the cubic structure and leads to the hcp structure.

Table 5. Some crystal structures of the metals in the periodic table and the ratio $\rho = c/a$ for the hcp structure.

Li bcc	Be hcp 1,567			
Na bcc	Mg hcp 1,624			
K bcc	Ca fcc	Sc hcp 1,594	Ti hcp 1,588	Zn hcp 1,856
Rb bcc	Sr fcc	Y hcp 1,571	Zr hcp 1,593	Cd hcp 1,886

On the other hand the increase of the charge of the nucleus leads to a whole shrinkage of the kernel closing the atoms and increasing the strength of the bonds. This last point is less sensible for the case of Sc, Y, Lu and La but important in the case of the hcp structure of Be and Mg as compared to the bcc structure of Li and Na. Indeed the relative increase of the charge of the nucleus is important in the both cases: it goes from one for three to one for four between Li and Be and to one for eleven to one for twelve between Na and Mg. It allows a large increase of the strength of the bonds and to go to eight to twelve nearest neighbours. Thus one has to keep the same approach to understand the hcp structure of Be and Mg.

The Table 5 gives equally the ratio $\rho = c/a$ of the two lattice constants of the unit cell. It most often exhibits a shrinkage of the lattice constant c with respect to the perfect packing with spheres giving $\rho = 1,633$. At the opposite the cases of Zn and Cd exhibit an expansion. The shrinkage shows for the six nearest neighbours in the direction of the equatorial plane a little smaller attraction through the equatorial windows than the attraction between the six other nearest neighbours through the azimuthal window. The attraction takes place mostly between the np electrons and the different windows of the neighbours. As there are more np electrons orbiting in the vicinity of the equatorial axis than in that of the equatorial plane one has to attribute the shrinkage of ρ to this aspect of the atomic dissymmetry. The cases of Zn and Cd have to be understood as the result of the occupancy of the ten nd electrons. Indeed there are two of them in the vicinity of the azimuthal axis closing in part the azimuthal window; since the interatomic attraction in this direction is smaller than perpendicularly.

Finally to supplement the interpretation of the dhcp structure of the lanthanum suggested in 5.1, suppose a synchronous bond for the $6s$ electrons along two of the axes of the O_1 or O_2 system Figure 8. To give to all the atoms a same spatial occupancy one possibility is to suppose that in these bonds the aphelions are pointed on the same side of the close-packing plane to which the atom belongs toward the perihelion of the other trajectory.

6.6 The La_2O_3 structure and the covalence

Consider the type structure of La_2O_3 oxide, Figure 13, initially studied in "Crystal structures and Bonds". It is equally the thermodynamically stable structure for the sesquioxide of Ce, Pr and Nd. It is characterised by the hcp lattice of the atoms of lanthanum. In this stacking one oxygen atom occupies the octahedral site and two others the tetrahedral site. The oxygen atom of the octahedral site is easily substituted by S, Se, Te, SO_4 and so on, that of the tetrahedral site is stable, strongly covalent and characterise in spectroscopy of absorption of the rare earths by a large shift toward the red [32],[33] in La_2O_3 and La_2O_2S . On the other hand

the importance of the (LnO) group or (Ln₂O₂) where the distance La—O is stable and close to 2.30 Å has been underline [34] pointing out a strong La—O bond.

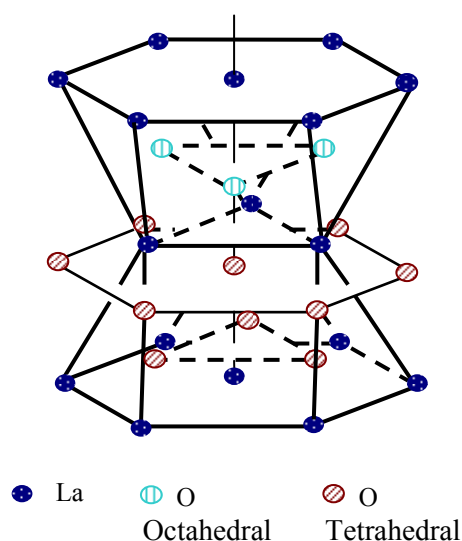


Figure 13. The La₂O₃ structure

Since the study "Crystal structures and Bonds" we have shown the role of bond of the xenon shell of the rare earth [25]; so it is preferable to attribute to this contribution the strong covalence of the oxygen of the tetrahedral site more than to the alone deepness of the 4*f* electrons. Furthermore it is allowed to suppose that the contribution of the xenon shell comes of the large eccentricity of the 5*p*,5*s* electrons, these electrons being attracted through the window on the nucleus of the oxygen atom, that one can write down: La → O; the direction of the arrow pointing out that the electrons of the lanthanum are those attracted by the oxygen. As a result the corresponding bonds will be shorter than those able to take place at the opposite in the vicinity of the perihelion; these distances favour the building of the two tetrahedral and octahedral sites. On the

other hand the greater stability of the compounds La₂O₂X with X= S, Se or Te with respect to La₂O₃ oxide leads to suppose a similar contribution between the *np*,*ns* electrons of the chalcogenides and the windows on the nucleus of the rare earths that one can write down La ← X. The increasing eccentricity with *n* of the trajectories *np*,*ns* leads to stronger and stronger bonds going from O to Te, thus the substitution of the oxygen by the others chalcogenides. This approach of the covalence opens a way for several other covalent structures as: ZnS, ZnO, CaF₂ discussing the charge of the kernels of the different atoms and the eccentricity of the trajectories of the electrons able to enter in bond with the kernel of a neighbour. The following study of the magnetite is a further example.

6.7 The Fe₃O₄ magnetite, the spinel structure and the notion of valence

A large number of compounds with the RM₂O₄ formula crystallize with the spinel structure. In this structure the atoms of oxygen occupy the position of an almost perfect cubic close-packing arrangement. Notice that in the ionic approach the oxygen ion has the largest volume and the lattice seems built on packing of these ions. In this fcc lattice the atoms of metals occupy two sites: one atom in the A tetrahedral site and two atoms in the B octahedral site. The building process of the crystal space from neutral atoms brings a new light for the Fe₃O₄ magnetite where iron occupies the two sites of the metals. Notice that in this approach the iron atoms have the larger volume, about the double to that of the oxygen.

During the first attempts to interpret the spinel structure the simplest seemed to attribute the tetrahedral site to the R metal and octahedral to M metal. However it shortly appeared difficulties concerning the size of the metal occupying the two sites. In this eventuality for MgFe₂O₄ and MgAl₂O₄ the magnesium the biggest of the two atoms or of the metallic ions would occupy the smallest site [36]. The study of the intensity of the ray of diffraction has led to suppose that the half of the B occupies for the two spinels. Consequently when the R atom

occupies the A tetrahedral site, the spinel is called normal and inverse if occupies the B site with one of the two M atoms.

In the case of the Fe_3O_4 magnetite, the equilibrium of valence leads to distinguish to types of iron atoms: two Fe(III) trivalent iron atoms and one Fe(II) bivalent iron atom. In the ionic approach the ferrous iron being smaller than the ferric iron it possible to propose an inverse structure spinel. With neutral atoms the size of the volume to distinguish the two types of atoms or the intensity of the rays of diffraction does not allow to decide of the inverse of normal character of the spinel. We need a different approach. On the other hand there is a need to understand how the crystal space is built with the spinel structure for this compound.

In "Crystal Structure and Bonds" [4] the comparison between the volumes of the monochalcogenides of rare earths and of the $3d$ metals shows the tetravalent character of different metals including iron and the existence of metal-metal bonds responsible of the valence. This result points out that metals with metal-metal bonds play an important role in the building process of the space. As a result of the short metal-metalloid distance, the tetrahedral coordination can be considered as more stable than the octahedral coordination with larger metal-metalloid distances. The existence of numerous radicals with the tetrahedral coordination as PO_4 , SO_4 , and VO_4 equally allows going in this way. Consider the inverse spinel NiFe_2O_4 , the iron with two $3d$ electrons less than nickel has windows on the nucleus more attractive imposing its tetrahedral coordination and leaving to nickel and to the other half of iron the octahedral site. Thus we are led to suppose that the space is built by the $[\text{FeO}_4]$ covalent groups and between them the other atoms of metal make cement. In this view one has to consider the magnetite as a normal spinel. The interpretation of the Curie constant is coherent with this approach [37]; it leads in Kemu/gat unit to two time the $C(\text{Fe}_B) = 5.55$ value and one time the $C(\text{Fe}_A) = 3.12$ value giving $C(\text{Fe}_3\text{O}_4) = 14.22$ as theoretical value for an experimental value of 14.2 and a spin value of 11.76 according to the classical model. The calculation of the μ magnetic moment to saturation to zero Kelvin degree is equally in agreement with this approach; supposing with Néel [39] an antiparallel coupling between the A and B sites it comes:

$$\mu_{\text{th}} = 2\mu(\text{Fe}_B) - \mu(\text{Fe}_A) \quad (6.6)$$

The magnetic moment of iron in the oxides can vary according to the electrons contributing [38]. For the magnetite and the nickel ferrite inverse spinel, the moments to consider are $\mu(\text{Fe}_B) = 4,6\mu_B$ and $\mu(\text{Fe}_A) = 5 \mu_B$. For the magnesium ferrite it comes $\mu(\text{Fe}_B) = 4,2\mu_B$ and $\mu(\text{Ni}_B) = 2,6 \mu_B$. the change of $0,4\mu_B$ between two iron moments correspond to the contribution of one of the two $3d_{3/2}$ electrons.

Table 6. Magnetic moments

RFe_2O_4	μ_{th}	μ_{exp}	$\mu_{\text{th-Néel}}$
Fe_3O_4	4.2	4,118	4
NiFe_2O_4	2.2	2,22	2
MgFe_2O_4	0.8	0,86	0

In the table 6, for $\mu(\text{Fe}_3\text{O}_4)$ the experimental value of 4,118 μ_B is that obtained by Pauthenet en 1983 on single crystal in the direction of easy magnetization and with magnetic field up to 180Koe [40]. The other experimental values are those from the thesis of Pauthenet [41]. Other values of magnetization of the ferrites are given by Goodenough [42]. The moment μ_{th} of the model of Néel is the sum of the contribution of one electron in Bohr magneton by single electron.

There is still to specify the valence of the atoms according to the site. The hypothesis of a four valence of iron in the monochalcogenides is connected to one or several metal-metal bonds. These bonds take place thanks to the $(n+1)s$ electrons and do not contribute to the equilibrium of the valence with the metalloid atoms. If we associate two of these bonds to the

iron atoms in the tetrahedral site, then this iron contributes to two units of valence of the oxygen atoms; for example as we have suppose it in section 5.2, the np,s shell of the iron atom of the tetrahedral site balance two unit of valence of one or two of the four oxygen atoms of the site. In this interpretation the iron of the octahedral site contributes then for three unit of valence of the oxygen atom of the site.

Thus it appears useful to distinguish two valence contributions: one determining the balance between the elements of the compounds expressed as "The combining or substituting capacity of an element with or to hydrogen", another determining the number of metal-metal bonds. But a contribution between identical atoms, if it gives information on the volume does not give information on the chemical composition. Thus this approach allows better understanding of the notion of valence resulting of the composition of the compounds and which was so useful in the building of our knowledge for chemistry and the structure of the atom as well.

7 Conclusion

Thus the Bohr-Sommerfeld quantum model completed by the interpretation of the doublets on the basis of Dirac's equation allows to describe the atomic space and then to propose a deeper understanding of numerous crystal structures. The door is open, there is still to pursue the exploration. It is always a deep joy to progress after to have been blocked by difficulties of which the overtaking seems to escape. It was during a long time the case of the magnetite where the logic imposes that two atoms identical initially keep the same properties if the space in which they are allows it.

Acknowledgements

Finishing this work it is a pleasure for me to thank the Professor Daniel Fargue who encourages me to express my understanding of the crystal state. I want also to express my gratitude to the Directeur de recherche Krishnan, with who I have discussed numerous subjects since almost forty years.

8 Appendix

To discuss about the spatial extension of the different electrons, consider their levels of energy; they are given by the following relation:

$$\frac{E_{n,k}}{m_0 c^2} = \left[1 + \frac{\alpha^2 Z_{eff}^2}{\left[\rho + \sqrt{k^2 - \alpha^2} \right]^2} \right]^{-1/2} - 1 \quad (8.1)$$

where Z_{eff} is the effective nuclear charge that is the Z atomic number reduced of the screening constant of the considered electron and α is the fine structure:

$$\alpha = \frac{2\pi e^2}{ch} \quad (8.2)$$

In introducing R the constant of Rydberg:

$$R = \frac{2\pi^2 m e^4}{ch^3} \quad (8.3)$$

The limited development of (8.1) gives:

$$T_{n,k} = -\frac{E_{n,k}}{hc} = \frac{RZ_{eff}^2}{n^2} + \frac{R\alpha^2 Z_{eff}^4}{n^4} \left[\frac{n}{|k|} - \frac{3}{4} \right] + \dots \quad (8.4)$$

As a function of the atomic number Z one has $Z_{eff} = (Z - \sigma)$ where σ is screening constant. Thus more the screening constant is important more the energy of the level is small and more the electron orbits far from the kernel of the atom.

9 References

- [1] Oudet X. et G. Lochak, J. Magn. Magn Mater. 65, 99-122 (1987).
- [2] White H.E., Introction to atomic spectra, McGraw-Hill Book Company, Inc. New York and London, (1934). For Runge's law see page 153.
- [3] Oudet X., Ann. Fondation Louis de Broglie, **29**, 493-512, (2004).
<http://www.ensmp.fr/aflb/AFLB-293/table293.htm>
- [4] Oudet X., , Ann. Chim. Fr., **8**, 483 - 507, (1983).
- [5] Oudet X., , Chim. Papers **51**, 304-309 (1997).
- [6] Voir la note de Prévot A.R., C.R. Acad. Sci., **268**, (1969).
- [7] Svabadváry F., "The Hystory of the Discovery and Separation of the Rare Earths" in "Handbook of Physics and Chemistry of Rare Earths, Volume 11-Two-Hundred-Year Impact of Rare Earths on Science" Editor: Gschniedner K. A. Jr and Eyring Leroy, North-Holand, (1988), tableau 1 page 53.
- [8] Broglie de L., "L'Électron magnétique", (Théorie de Dirac), Hermann et Cie (1934). Pour le calcul des différentes projection du moment cinétique voir pages 237 à 240.
- [9] Oudet X., J. Magn. Magn Mater. **98**, 298-331(1991).
- [10] Oudet X., Ann. Fond. Ann. Fondation Louis de Broglie, **20**, 473-490, (1995)
- [11] X. Oudet, Ann. Fond. Ann. Fondation Louis de Broglie, **26**, 639-651, (2001)
<http://www.ensmp.fr/aflb/AFLB-264/aflb264p639.htm> En français and in English.
- [12] Gallais F., « Chimie minérale théorique et expérimentale (chimie électronique) », Masson, (1950).
- [13] Kittel C., Introduction to Solid State physics 3rd edition, Johniley and son, (1967).
- [14] Wykoff, W. G., "Crystal Structures" Volume 4, second dition, Interscience Publishers (1968).
- [15] Jayaraman A., Klement W., Jr and Kennedy G.C. Phys. Rev., **132**, 4, 1620, (1963).
- [16] Jayaraman A., Physics of Solids at high pressures, Ed. CT. Tomizuka, R.M. Emerick, 1965, Academic Press N.Y. and L., Rare Earth Metals at High Pressures and Temperatures
- [17] von Laue M., In : the introduction to "International Table for X-Ray Crytallography" Volume I, 1-5, The international Union of Crytallography, The Kynoch Press, Birmingham, England (1969).
- [18] Oudet X., "Le Point sur le Quantique" Publié dans "Courants, amers, écueils en microphysique; Direction in Microphysics", 299-310, 1994, édité par Christian Cormier-Delanoue, Georges Lochak and Pierre Lochak, Bibliothèque des Annales de la Fondation Louis de Broglie, 23 quai de Conti, 75006 Paris, France.
- [19] Guinier A., « Théorie et thechnique de la radiocristallographie, page 141, Dunod (1956).

- [20] Oudet X., Thèse n° 853, Université de Paris, Faculté des Sciences d'Orsay, 10 novembre 1971.
- [21] Chemistry: WebElements Periodic Table: <http://www.webelements.com/>
- [22] Wyckoff, W. G., "Crystal Structures" Volume 1, second dition, Interscience Publishers (1969).
- [23] Chernick C.L., et al., Science 138, 136-8, (1968).
- [24] Anderson S., Acta. Chryst. B 35, 1321-4, (1979).
- [25] Oudet X., « Theoretical and experimental aspect of the valence fluctuation and heavy fermion », Editors : L.C. Gupta and S.K. Malik, Plenum Publishing Corporation, 637-640, (1987).
- [26] Mishra N.C., Oudet X., Physica, C212, 465-9, (1993).
- [27] Oudet X., Ann. Fondation Louis de Broglie, 22, 409-421 , (1997).
- [28] Bridgman P.W., Z. Kristall., 67, 363-376, (1928).
- [29] Jacobs, Phys. Rev., 54, 468-474, (1938).
- [30] Pistorius C.W.F.T., Snyman H. C., Z. Physk. Chem., 43, 1-10, (1964).
- [31] Pistorius C.W.F.T., Nature, 204, 467-8, (1964).
- [32] Jorgensen C.K., Progress. Inorg. Chem. 1962, 4, 73.
- [33] Caro P. and Derouet J., C.R. Acad. Sci., 1970, 271-C, 1370-3.
- [34] Caro P., C.R. Acad. Sei., 1966, 262-C, 992-5.
- [35] Evdokinova V.V., Vereshshagin L.F., Fiz. Tverd. Tela, 4, 1965-6, (1962); Translation in Sov. Phys. Solid State, 4, 1438-9, (1962/3).
- [36] Barth T.F.W. and Posnjak E. J., J Washington Acad. Sci., 21, 255-8, (1931), and Z. Kristallogr., 82, 325-341, (1932).
- [37] Oudet X., J. Phys. IV France, C1-177-C1-178, (1997). En consultant ce travail je constaye une erreur pour Fe ce n'est pas $C = 5.45$ qu'il correspond à un moment $3.2\mu_B$, mais $C = 5.55$ ce qui donne $C(Fe_3O_4)_{th} = 14.22$ au lieu de 14.02.
- [38] Oudet X., J. Mag. Mag. Mat. Vol 272-276P1 pp 562-564, proceeding of ICM-2003, 2004, Edited by D. Fiorani and L. Pareti ou en français Ann. Fondation Louis de Broglie, 26, 353-366, (2001).
- [39] Néel L., Ann. de Phys. 3, 137-198, (1948).
- [40] Pauthenet R., High Field Magnetism, M. Date (editor), North-Holland Publishing Company, 77-86, (1983).
- [41] Pauthenet R., Ann. de Phys., 7, 710-747, (1952).
- [42] Goodenough J., "Magnetism and the Chemical Bond", Interscience Publishers, John Wiley and Sons, (1963)

Reçu le 3 avril 2007, modifié le 25 juin 2007 et le 23 juillet 2007.

Contents

1 Introduction	1
2 The periodic table and the quantum numbers	2
3 The spatial distribution of the <i>ns</i> , <i>np</i> , <i>nd</i> and <i>nf shell</i> .	4
3.1 The kernel of the atom and its outer electrons.	7
3.2 Windows upon the nucleus, covalence, ionicity and overlapping bonds.	7
4 The synchronous bond	9
4.1 The synchronization of the electronic motions	10
4.2 Synchronization, transfer of thermal energy and disorder	10
4.3 Synchronization and chemical disorder	11
4.4 The limits of the notion of ionicity.	11
5 The crystal and the atom	11
5.1 Disorder and crystal symmetry	12
5.2 The crystal and the valence	14
6 Crystal Structures and Bonds	16
6.1 The body centred cubic	16
6.3 The cfc \rightarrow cc transformation.	20
6.4 The ClCs and ClNa structures	20
6.5 The hexagonal close-packing structure.	21
6.7 The Fe ₃ O ₄ magnetite, the spinel structure and the notion of valence	23
7 Conclusion	25
8 Appendix	25
9 References	26