

From Ln valence to that of 3d¹

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We demand the short-term results and are often too impatient to explore its later consequences. We like to define things in precise terms; and the definition betray us into fixed positions from which we cannot withdraw.

Morris West, "The Ambassador", 1965

Abstract. The valence was defined as the capacity of combination or substitution with or to the hydrogen. The existence of rare gas compounds leads to consider the possibility for the electrons of the outermost shell of a metal in a compound, to be those entering in bond with neighbor atoms and stabilizing the observed valence.

1 The rare earths metals

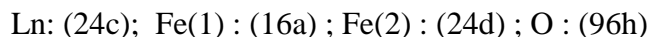
We know that the rare earth elements have mainly the valence three, a situation very different of that of the 3d elements which exhibit various possibilities. To understand this difference, we have to discuss the origin of the valence three of the rare earths. The two first valence states of the lanthanum have the same origin than for the barium, element just before cesium and lanthanum. They are the result of the two 6s electrons appearing after the xenon. On the other hand the filling of the 4f shell starts after those of the 5s, 5p, 4d and 6s shells that is an amount of twenty electrons. Then it seems difficult to involve a 4f electron which is protected by all these electrons to explain the valence three of La. It is for this reason that in the old text books, the additional electron appearing with the lanthanum is supposed to be a 5d electron and also for some other elements of the rare earths [1]. This hypothesis is now more or less forgotten but not fully. Considering the corpuscular model [2] an alternative approach is to suppose that it is the xenon shell, with its electrons gravitating in different directions of possible bonds, which leads to the third valence state of the Ln. Indeed we know since about fifty years that the xenon as some other gas call "inert" has valence and bonds properties [3-5]. As a result it is possible to consider that the two 5s electrons of the elements following the xenon can contribute to the bonding properties.

¹ This study results of discussions on ResearchGate.

In the compounds as the oxides, the valence can be understood as it follow: for two elements giving a compound the ratio of the number of atoms of one of them is inversely proportional to the charge of the nucleus of the other. Thus one has to understand the chemical combination as the probability of electronic interactions with the respective charges of the nucleus of the considered compound. For La_2O_3 , the charge three of the nucleus is visible through the equatorial and polar windows [8], so they can attract three electrons of oxygen atoms, for example two $2s$ $2p$, on the other hand the charge of the nucleus of the oxygen is two it can attract two electrons from the atoms of the metal. The stoichiometry depends on the conditions of synthesis, but the statistical aspect leads to a certain probability of discrepancy. The electrons of lanthanum able to enter into bonds with oxygen atoms are the two $6s$ and one of the two $5s$. This approach is corroborates with the high T_c superconductors as $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ where the bivalent barium replace the trivalent lanthanum [6]. For the other rare earths the increase of the nucleus charge is neutralized with the other $4f$ electrons which behave as screen and the valence stays generally three that is different from the $3d$ metals.

The importance of this new approach is that the oxygen in the tetrahedral site of La_2O_3 with a four coordination of lanthanum allows the interpretation of the bixbyite, the structure of Er_2O_3 and many other compounds. The space groupe is T_h^7 (Ia3) with (Er1) in (8a), (Er2) in (24d) and O in (48e). The resulting structure is most easily thought as an incomplete cubic-close packing of the oxygen atoms, the metallic atoms are distributed as are the cerium atoms in CeO_2 which has the CaF_2 structure [15]. The tetrahedral coordination induce with the two $5s$ electrons together with the two $6s$, is the clue of the structure.

Another confirmation of this approach can be propose with the garnets $\text{Ln}_3\text{Fe}_5\text{O}_{12}$. The study "Atoms and crystal structures" has allowed to show the normal spinel character of the magnetite Fe_3O_4 [8]; the logics of this study leads to establishe that in the case of the garnets $\text{Ln}_3\text{Fe}_5\text{O}_{12}$ the tetrahedral and octahedral sites are associated to different properties of the iron. The sites of the garnets are:



That is : $3\text{Ln: (24c); 2 Fe(1) : (16a) ; 3 Fe(2) (24d)}$

The two sites of the iron lead to suppose like for the magnetite the formation of FeO_4 group with a redistribution of the valence. In this approach the tetrahedral site must be considered as tetravalent. We find there a known property of numerous silicates and germanates garnets. What is then the corresponding valence for the two other metals? The balance of the valences leads to take II for Ln and III for octahedral Fe. The existence of silicates as $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ corroborates this interpretation [9]. It shows the bivalent character of the dodecahedral site and the trivalent character of the octahedral site. The garnet $\text{Ca}_3\text{Y}_2\text{Ge}_3\text{O}_{12}$ exhibits the same characteristics [10]. Considering the magnetic properties we have already shown the two possible different magnetic contributions of the tetrahedral and octahedral sites of iron [11]. Furthermore recently the substitution of Sm by Ca in $\text{Sm}_3\text{Fe}_5\text{O}_{12}$ garnet strongly corroborate the valence two of Sm in the SmIG [12].

A contrario, I wish to underline that the attempt to synthetize $\text{Tl}_3\text{Fe}_5\text{O}_{12}$ has given negative results [13]. It is evident that with bivalent Ln and a Xenon shell role in the stability of the LnIG this attempt was hopeless.

2 The 3d metals

Thus, if with the Ln, it is the xenon shell which stabilizes the valence, one has to attribute to the argon shell, the stability of the different valence state of the 3d metals. This is suggested by the calculus of the magnetic momentum where the 3d electrons stay on their atom [14] and also with the existence of complex as $K_4[Fe(CN)_6]$ which can be compared to XeF_6 [5].

Considering the 3d metals, for example the iron, one has to attribute the valency two to the two 4s states. Let us now consider the Ar shell and its two 3s states, up to now we always have supposed that the valence three is the result of the two 4s electrons and of one electrons 3d. The comparison with the Ln, leads to suppose a similar behavior that is a contribution of the two 4s electrons and also of one of the eight electrons 3sp which contribute to Fe_{III} . On the other hand for Fe_3O_4 and the tetrahedral site, we can suppose a contribution of the two 4s and also of two of the eight 3sp of the iron which favor the tetrahedral occupation of the iron, that is the normal spinel structure giving Fe_{IV} , thus the valence four of the iron that one can compare to XeF_4 [5]. Regarding the iron occupation of the octahedral site one has to suppose that it is stabilized with bonds from the argon shell that one can compare to XeF_6 [5].

This approach allows to propose an explanation of the spinel structure. For the Fe_3O_4 it is built on the two 4s electrons and two of the eight 3sp electrons of the argon shell. But these electrons are still present in the other 3d elements, giving the same normal spinel structure with Co_3O_4 . Consider now $NiFe_2O_4$ which has an inverse spinel structure, the charge of the nickel nucleus is higher than that of the iron, the additional electrons increase the screening of the nucleus and as a result the ability of the argon shell to develop bonds leading to the inverse character of this spinel. The study of the spinel structure from the trajectories of the electrons is thus corroborated.

Now Mn_3O_4 has the structure hausmannite, which is a spinel structure with a tetragonal distortion. We know that the cubic structure result always of a disorder [7]. The distortion of the hausmannite can be attribute to the result of a lower disorder, probably that the $4s^2$ and $3s^2$ electrons all orbit with different planes but all these planes with an angle of 45° with the same plane equatorial plane (see [2], figure 3 and table III). One possible explanation is that this plane stays the same for almost all tetrahedral Mm atoms.

3 Conclusion

Thus according to this approach the bonds between one atom of metal 3d or Ln and one oxygen atom are the result of bonds with electrons of the outermost shells of the atom of metal and the nucleus of the oxygen atom, the same approach can also be used for the 4d and the 5d.

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