Why is it Time for a New Clarifying Approach in Crystal Chemistry?

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The first crystal structure determination (NaCl) from X-ray diffraction data, was reported in 1913. Since then, the ionic model (Goldschmidt, Pauling) has been used to justify the structures of inorganic compounds. This model describes the structures as a close packing array of big anions held together mainly by electrostatic interactions. Small cations occupy tetrahedral/octahedral voids depending on their ionic radii. Although widely used during one century to describe structures, it has not been able to explain, neither to predict the structures of oxides. As it has been asserted by the mathematician René Thom, "To predict is not to explain" [1]. Regarding predictions, the great efforts accomplished by *ab initio* theoretical calculations, based on genetic algorithms have not led to satisfactory results. Their predictive power is poor and the structures remain unexplained. During the last 25 years, the visual analysis of crystal structures revealed unexpected features that offer *true challenges* to the traditional models accounting for the bonding in solids. They will be discussed in this lecture:

- It is assumed that the small radius of Si^{4+} cations induces its tetrahedral coordination. Only, under pressure, the Si can reach the CN = 6. However, Si atoms are hexa-coordinated in some compounds at normal pressures.
- The finding of Wondratschek *et al*. that shows that the cationic array in apatite $Ca_5(PO_4)_3F$ is identical to that of the Fe_5Si_3 alloy has not yet been explained [2].
- A new relation between oxidation and high pressure has been found by Vegas *et al.* [3].
- The Zintl-Klemm concept has been applied to explain the Si-skeletons of silicate polyanions and could be the universal key to interpret many of the known structures.
- It has been found that *the structures of the elements are maintained when they form more and more complex compounds and are crucial for understanding the structures of both alloys and oxides. [This observation is related to the new concept of Chemical Pressure.]*
- Finally, we will make a passing inspection of these challenges through the results obtained from theoretical calculations (ELF) as well as from the Thom's Catastrophe Theory [1], showing the possible connection between the Thom's Sedimentation Concept and the Zintl-Klemm Concept.

[1] Thom, René & Noël Emile. *Prédire n'est pas expliquer.* "Editions Eshel: Paris (1991).

[2] Wondratschek, Hans; Merker, Ludwig & Schubert, Konrad (1964) https://doi.org/10.1524/zkri.1964.120.16.393

[3] Vegas Ángel. "*Modelos estructurales de cristales inorgánicos".* (2020) http://hdl.handle.net/10259/5647