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CHEMISTRY

STRUCTURAL MODELS OF INORGANIC CRYSTALS

FROM THE ELEMENTS TO THE COMPOUNDS

Ángel Vegas



Editorial
Universitat Politècnica
de València

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By

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*To Diego, Jaime
and Carmen*

Acknowledgments

This book is the result of the effort made by a few collaborators and myself to deepen the understanding of crystal structures of inorganic solids. I wish to express my sincere thanks to Prof. Carlos Otero-Díaz who showed me the way initiated by his master B. G. Hyde and by M. O'Keeffe in the search for new models to describe the structures of solids. I am indebted to him for his permanent support and friendship.

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The discovery of the relationship linking oxidation and pressure in 1994 opened a new field of research. The first experiments aiming to demonstrate the soundness of this concept were carried out, on alkali sulphides, during my six-months visit to the Max-Planck Institut für FKF (Stuttgart) in 2000. Prof. Martin Jansen facilitated that stay with scientific and financial support, for which I wish to express my thanks. The aid provided by his co-workers to perform the synthesis and the high-pressure experiments is greatly appreciated.

In 2003 David Santamaría-Pérez joined our project. At that time, the experiments on alkali sulfides (Rb_2S and Cs_2S) under pressure were continued in collaboration with the MPI team. In addition, the invitation from Prof. Julien Haines and Prof. Olivier Cambon to visit the University of Montpellier (France) allowed us to perform new in-house high-pressure X-ray diffraction experiments. We are indebted to them for their friendship and collaboration.

In his Ph.D. Thesis, David Santamaría-Pérez extended the Zintl-Klemm Concept to the polyanions of aluminates and silicates. This fruitful extension of the Zintl's Concept served to put the structures of aluminates, silicates, phosphates, etc. on a common basis. Thus far, they had only been classified in a taxonomic way. David's Ph.D. Thesis will remain as a milestone in the field of crystal chemistry. His work and help is highly appreciated.

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When this book was being prepared for edition in the series IUCr/OUP, I was fortunate in exchanging relevant thoughts on science and crystallography with

Prof. Davide Viterbo (UPO, Italy) as Chair of the Book Edition Committee of the IUCr, who sadly passed away on 20th May 2017. His memory will remain forever.

At the beginning of my carrier as a scientist I could enjoy the unforgettable company of my colleague and friend Dr. Julián López de Lerma (†1992). I miss the many hours of discussion we spent together on the essence of research and science.

Finally, my sincere acknowledgment to the University of Burgos, especially to Prof. Jordi Rovira, for providing me with the title of Honorific Professor and thus helping me avoid become a homeless scientist.

About the author

Ángel Vegas Molina was born in the province of Toledo (Spain). He graduated in Chemistry in 1970 at the Complutense University of Madrid, where he also earned his Ph. D. in February 1975. After performing postdoctoral stages at the Crystallography Laboratory of CNRS in Grenoble (France) and at the University of Düsseldorf (Germany), he earned in 1978 a permanent researcher position at the Institute for Inorganic Chemistry "Elhuyar" of CSIC in Madrid (Spain). In 1988, he moved to the Institute for Physical Chemistry "Rocasolano", also belonging to CSIC. During his researcher career at CSIC, he has visited as an invited researcher different institutions mainly in Europe. In the 80's, he did a several stays at the Technische Hochschule Darmstadt (Germany). In 2000, he did a six-months stay at the Max Planck Institute for Solid State Research in Stuttgart (Germany). In 2005, he visited the CNRS of Montpellier (France). Since 2012 up to his retirement in 2015, he was ascribed as a researcher at the University of Burgos (Spain) where he remains as Honorary Professor.

Dr. Vegas has published 116 articles, 5 book chapters and has been editor of a volume in the prestigious collection "Structure and Bonding" of the editorial Springer. He has supervised three Ph. D. Thesis and has given ca. 70 lectures in Universities and Research Centres all over the world as well as Post-graduate courses in Spain, Venezuela, Argentina and Morocco.

Dr. Vegas initially worked experimentally in the Crystal Structure Determination of inorganic compounds and, in the early 80's, he worked in the determination of the absolute electron density distribution of materials, in particular MgCO_3 . In 1986, he decided to quit the experimental determination of crystal structures and devote his time to think about the reasons determining why crystal structures are as they are as well as to search new models that improve the explanation of the structures of inorganic compounds. In 2000 and 2005, he participated in x-ray diffraction measurements under high-pressure, which demonstrated the validity of the *relationship between oxidation and pressure*.

Dr. Vegas' four most notable scientific contributions are: 1) The discovery of the relationship between Oxidation and Pressure, which allows to understand the structures of metal oxides as pressurized phases of the metallic elements. 2)

The extension of the Zintl-Klemm concept, which accounts for the skeletons of thousands of compounds such as aluminates, silicates, phosphates, germanates, arsenates, etc. 3) The deepening in the concept that cation subarrays in oxides preserve the structures of either elements or the constituent alloys, so that oxides can be defined as real oxygen-stuffed alloys. 4) The discovery that elemental structures are the key to understand the more complex structures of oxides.

Prologue

*The longer I live, the more I realize the impact of attitude on life.
Attitude, to me, is more important than facts.
It is more important than the past, the education, the money, than circumstances,
than failure, than successes, than what other people think or say or do.
It is more important than appearance, giftedness or skill.
It will make or break a company... a church... a home.
The remarkable thing is we have a choice everyday
regarding the attitude we will embrace for that day.
We cannot change our past... we cannot change the fact that people
will act in a certain way. We cannot change the inevitable.
The only thing we can do is play on the one string we have, and that is our attitude.
I am convinced that life is 10% what happens to me and 90% of how I react to it.
And so it is with you... we are in charge of our Attitudes.*

Charles R. Swindoll

It is a pleasure to me and a great honor to write the prologue of this book of my friend and colleague, Dr. Ángel Vegas, who shows in this book the vast knowledge he has acquired during thirty years of hard work and that now, that he is retired, shares completely with us as a legacy to future generations.

I met Dr. Vegas eighteen years ago at the Max Planck Institute for Solid State Research in Stuttgart (Germany), where I was a postdoctoral researcher thanks to a "Marie Skłodowska-Curie" fellowship of the European Union and where Dr. Vegas did one of his many international research stays. During the coffee breaks we had he talk to me about his new ideas about the chemical bond and how such ideas led him to Stuttgart in order to perform a series of high-pressure experiments in a family of compounds that will allow him to verify his predictions. I was surprised that his ideas elicited such a skepticism in the scientific community and that many journals with high impact factor closed their doors at his ideas, despite the observed structural relationships between different compounds exhibited the goodness of the affirmations, and even predictions, of Dr. Vegas.

The idea of Dr. Vegas that was more captivating to me, as a Solid State physicist devoted to the study of Materials at high pressures and expert in pressure-induced phase transitions, was the equivalence between pressure (as a physical magnitude) and oxidation (as a chemical pressure). I was struck to know that crystalline structures present at high pressure in simple elements or in their metallic alloys could be observed at room pressure or at low pressures in the oxides of such elements or of their alloys. The experimental confirmation of this paradigm in a number of compounds clearly showed that Dr. Vegas was right and suggested him the idea that the atoms of the different element do not lose their memory despite being surrounded by atoms of different elements; i.e., it is as if the different atoms could recognize each other and reach an agreement to preserve, although partially, its original identities.

Fortunately, those talks in Stuttgart derived with time in a deep friendship that allowed me to get closer to Dr. Vegas' ideas. In particular, he showed me the Zintl-Klemm concept, and I remember how I was struck when the generalisation of this concept, proposed by Dr. Vegas, revealed itself as a previous step to understand the crystal structures of a great number of compounds. Thanks to the generalisation of the Zintl-Klemm concept, Dr. Vegas has been able to infer that the crystal structure of a given compound is the result of a resonance among several crystalline structures. In other words, the crystalline structure of a given compound derives from the resonance of the electron charge densities present in the crystalline structures of several isoelectronic compounds related to the given compound.

On the light of the above-mentioned facts, Dr. Vegas' work deserves the greatest respect and the highest praise. Fortunately, he has found the collaboration of a few but renowned colleagues who have helped him in his noble and hard task. As an expert in Crystal chemistry, Dr. Vegas has studied the similitude's and differences between the crystal structures of the elements and of the cationic subarrays in a number of compounds. In particular, he has analyzed the topology of the crystal structures and the values of the interatomic distances and has provided clear evidence that the crystal structures of compounds bear a close relationship with the crystal structures of the elements that form part of these compounds. Here comes the subtitle of the present book: "From the elements to the compounds".

The knowledge that Dr. Vegas has acquired during his long scientific career have allowed him to dip into the concept of the chemical bond and have led him to question the current paradigm of the ionic bond model formulated by Goldschmidt and Pauling, and based in the idea of cations and anions; i.e., atoms eager to lend or borrow charge. The questioning of the fundamentals of the ionic bond model, allows one to understand the skepticism with which the scientific community has received Dr. Vegas' ideas. However, I encourage the readers to

study this book, which will allow them to better understand Dr. Vegas' ideas than in the many individual scientific papers that Dr. Vegas has published. I am pretty sure that this book won't leave any reader indifferent and that this book will be part of the basic texts of chemistry at pre-graduate level in the future.

It is often said that Spain is a "Land of Quixotes". In this case, we are in front of one of them. Not least, Dr. Vegas was born "*In a village of La Mancha, the name of which I have no desire to call to mind...*", the initial words of Cervantes' book. In fact, one could establish a certain parallelism between Dr. Vegas' life and that of the ingenious Nobleman Don Quixote of La Mancha. Don Quixote devoted his life to fight for the justice, against tyranny, embodied in the windmills that became giants. In a similar way, Dr. Vegas' work has not been fully recognized, it has been systematically underestimated both at a national and international level, and has bravely struggled for thirty years to defend his ideas in front of a scientific community that is resistant to change the paradigms related to the chemical bond in inorganic solids. Dr. Vegas has been out of the scientific mainstreams and has struggled against the tyranny of the scientific fashions, the big headlines, and big research groups managing big budgets and a lot of resources, as well as conditioned by Editors of the many of the most prestigious journals and publishers. Moreover, in the same way that the ingenious Nobleman Don Quixote of La Mancha struggled to bring justice to the world with the only help of his loyal squire (Sancho Panza) and a hungry horse (Rocinante), Dr. Vegas has given us a lesson about how to make groundbreaking science with a few human and material resources; i.e., with the collaboration of a few friends and colleagues and with the only access to scientific literature and to crystallographic databases. These conditionings have contributed to the publication of this book, with the support of one of his friends, at the press of the Universitat Politècnica de València; a university that is currently renowned by Chemical Engineering, Agronomy and Food Technology. Therefore, here is planted the seed that will blossom and grow in the future... like orange trees grow around us.

Valencia (Spain), November 2018.

Prof. Dr. Francisco Javier Manjón

*Full Professor of Applied Physics
Universitat Politècnica de València*

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Preface

On April 21st, 1912, in Munich, Walter Friedrich and Paul Knipping carried out an experiment designed by Max von Laue, which sought to demonstrate that crystals could diffract X-rays. The idea of diffracting capability by crystals was conceived by Laue, after discussions with Paul Ewald who told him his ideas about the lattice character of the crystalline aggregates (called *crystals*).

Just a year later, in 1913, W. H. Bragg and his son W. L. Bragg, resolved the first crystal structure by X-ray diffraction in London. It was the cubic structure of NaCl that, surprisingly, coincided with the model that Barlow had predicted in 1883.

After a century of experience, we can proclaim that these experiments led to one of the most significant discoveries in physics. The ability to determine crystal structures has been a major contribution to the knowledge of condensed matter, with a breakthrough in solid state physics, in mineralogy, in all fields of chemistry (organic, inorganic and metal organic) and, later, in the structural determination of biological macromolecules (proteins, DNA, viruses, etc.). In recent years, we have even seen the resolution of structural cell components (corpuscles) as complex as ribosome. The results have been: ~ 500,000 entries in the crystallographic databases (CSD, PDB, ICSD and PCD), which contain the work of thousands of crystallographers worldwide in the last 100 years.

The importance of crystallography is not limited to the resolution of the crystal structures. Advances in experimentation also helped solve structures of materials with low crystallinity such as polymers, amorphous materials or modulated structures with immeasurable cell parameters. In this field, we must outline the contribution of the convergent beam electron diffraction (QCBED) that together with the high-resolution electron microscopy (HREM), allowed for the structural determination of microcrystals.

The breakthrough in structural determination was due to great facilities such as neutron sources in nuclear reactors, the most recent neutron facilities and the third-generation synchrotrons. In the latter, high intensity pulses of up to femtoseconds, have led to progress in the knowledge of the structural dynamics,

kinetics of reactions, reaction mechanisms and phase transitions. We would be remiss if we didn't mention the new possibilities opened up by new sources such as XFEL (X-ray Free Electron Laser).

The progress mentioned in these new X-ray sources, together with the development of new codes for data collection and structure determination, have made of structural solution almost a routine process.

We must also highlight the advances provided by the synchrotron diffraction studies under conditions of extreme pressure and/or temperature. In the past 20 years, new phase transitions have been discovered; some of them have represented real challenges to existing theories and paradigms in current chemistry. This is a point to which we will devote special attention later in this book.

All this material has aided in developing evolutionary algorithms, which, together with new QM calculation codes, have promoted the prediction of new crystal structures at ambient conditions and under extreme, high-pressures as well.

This text is aimed at students as for M. Sc and PhD students, although some students in their final year of Grade could also benefit whenever they have acquired the necessary background in inorganic crystal chemistry. It is assumed that the reader is familiar with concepts such as Pauling's ionic bonding model, which interprets the structures of ionic solids as composed of anions and cations whose relative sizes are considered as one of the main factors determining their structures. It is here where the reader will find dissenting ideas, which hopefully will serve to better understand the structures. These ideas are only now gaining ground.

The main reason for this dissention is that the ionic model has not been able to explaining why the structures of inorganic solids are as they are. Following C. A. Coulson, any bonding theory should provide a satisfactory explanation of both energy and structure of a given compound. It is clear that the ionic model, based on the rules of the radius ratio, was insufficient to achieve that goal.

Throughout the text, we will make a survey of the alternative ideas. We will begin describing the pioneering work by O'Keeffe and Hyde (1985) in which the structures are described as oxygen-stuffed alloys. Subsequent works (1986-2016), by several authors, have provided new insights that are truly challenging. Among them, we can mention: the maintenance of the topology and distances of the metal structures in their oxides, the correlation between oxidation and pressure and the applicability of the Zintl-Klemm Concept to the cation arrays in oxides. In all of them, the cation arrangements are regarded as the determining factor of the structure.

These new ideas are combined with older concepts that usually concern molecular chemistry. Among them, the Hoffmann's isolobality concept, hypervalency, resonance structures, etc. What we are proposing in this text is a new way of looking at crystal structures by joining concepts that, up to now, had been limited to the molecular chemistry on one hand or to the solid state chemistry on the other hand.

The structures are completely dissected, discovering structures existing in simpler compounds, even finding fragments of the elemental structures of their components: an autopsy that allows us to perceive the structures in a holistic way.

In the last chapters, calculations of the ELF provide new data on why both bonding pairs and lone pairs can be identified with the O atoms in many of the structures considered. Throughout the text we have attempted to explain the structures in a simple way. The word "explanation" can be assigned a wide, sometimes ambiguous meaning. Contrarily, we try to describe the structures in terms of the simplest real arrays, i.e. *the elemental structures*.

This book is not aimed as a comprehensive description of crystal structures but to providing new insights that the readers can use for analyzing structures of interest for their research and/or teaching. It is worth mentioning that visualizing these structures and discovering within them their multiple components *is not an easy task*. Discovering how the different components complement each other and interconnect has required much effort and patience, which will facilitate the reader understanding of other compounds.

Thinking in teachers and researchers, a basic knowledge in handling Crystallographic Databases and the codes used to represent the crystal structures are all-helpful in deepening the understanding of ideas developed in this text in the unveiling of new structural relationships.

In this respect, the wealth of structural data offer immense possibilities for progress in the establishment of the laws governing the formation of structures and their resulting properties. The latter are less explored but are now starting to be "*visited*" by some crystal chemists. We align ourselves with the statement from Jack Dunitz, when he said that, "*Crystal Structure Data Bases contain hundreds of thousands of answers waiting for questions*". Some of the questions we have posed to both ICSD and PCD and some of those answers will be found by the reader in this book.

Madrid, 11th July 2012
Festivity of St. Benedict of Europe

List of abbreviations

A

- AIM** Atoms in molecules
AMM Anions in Metallic Matrices Model

B

- b.c.c. body-centred cubic
b.c.t. body centred tetragonal
BP Bonding pair
BS Bragg-Slater Model

C

- CN** Coordination Number
CSP Crystal Structure Prediction

D

- DFT** Density Functional Theory
d.h.c.p. double hexagonal close-packing
dist. distorted
DOS Density of States

E

- E** Electron Pair
ED Electron density
ELF Electron Localization Function
EZKC Extended Zintl-Klemm Concept

F

- f.c.c. face-centred cubic

G

- GP** Goldschmidt-Pauling Model

H

- h.c.p. hexagonal close-packing
hp high pressure
ht high temperature
HP High pressure
HT High temperature
HVI Hypervalent molecules of the type I
HVII Hypervalent molecules of the type II

I

- IUCr** International Union of Crystallography

L

- LAPW** Linear Augmented Planar Waves
LP Lone pair

M

- MEM** Maximum entropy methods
MO Molecular Orbital

N

- NMR** Nuclear Magnetic Resonance
NNM Non-nuclear maxima

O

- OKH** O'Keeffe and Hyde
OPC Oxidation-Pressure Concept

P

- PTE** Periodic Table of the Elements

Q

- QCBED** Quantitative Convergent Beam
Electron Diffraction
QM Quantum mechanical

S

- s.c. simple cubic
s.h. simple hexagonal

T

- TDS** Thermal Diffuse Scattering
tf thin film

U

- ULat** Lattice Energy

V

- VB** Valence Bond
VBT Volume-based Thermodynamics
VSEPR Valence Shell Electron-Pair Repulsion

X

- XRD** X-ray Diffraction
ZKC Zintl-Klemm Concept

CHAPTER 1

The basis of the classic crystal chemistry

1.1 Introduction

Crystal chemistry is a branch of science that studies atomic arrangements in crystals and the relationships between them. It was developed through experimental determination of the first inorganic crystal structures that were solved and hence, has dealt almost exclusively with inorganic solids, known as “ionic compounds”.

Many of these earlier structures were those of simple inorganic compounds such as NaCl, ZnS, SiO₂, TiO₂, CaF₂, etc. In the 1920's, when the first ideas about chemical bonding were drafted, chemists and physicists began investigating the formation of such closely packed structures of NaCl, which had been predicted by Barlow, in 1889 [1]. We can compare his blind prediction with Bragg's three decades later. Both drawings are in Figure 1.1.

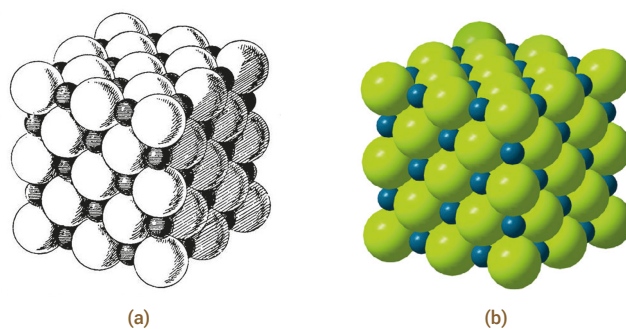


Figure 1.1 (a) Structure of NaCl as predicted by Barlow [1] [Reproduced from Barlow (1898), Figure 8]. The prediction was limited to the spatial distribution of Na and Cl atoms but not to their dimensions. (b) Representation of the structure determined by X-ray diffraction by the Bragg's (1913). Only in the latter case do we know that the parameter of the cubic unit cell is $a=5.625 \text{ \AA}$.

The experimental determination of the simple structures mentioned above led to the development of chemical and physical models, which proposed to explain these structures. These are known as bonding models. In the early stages, it was thought that inorganic solids, mostly oxides and halides, consist of positive ions

(cations) and negative ions (anions) whose opposing forces in the right structural arrangement would stabilize the structure by means of electrostatic forces. From this, the name “*ionic model*” was derived to describe this bonding model. As C. A. Coulson [2] states in his classic book “*Valence*”, any bonding theory must account for two observable facts: the energy and the structure. Therefore, in these first chapters, we will examine the extent in which the ionic model fits these two requirements.

1.2 The energy calculation

The early ionic model suggested that inorganic crystals were made up of anions and cations held together by electrostatic interactions. From these models Born and Landé (1918) concluded that the energy released when anions and cations came together to form the compound was the lattice energy U_{Lat} . The predominantly electrostatic contribution of lattice energy was quantified by the equation:

$$U_{Lat} = \frac{N M Z^+ Z^- e^2}{4\pi\epsilon_0 d_0} (1-1/n) \quad (1.1)$$

where N is Avogadro’s number, M the Madelung constant, Z^+ and Z^- the nominal charges of cation and anion respectively, e is the charge of the proton, ϵ_0 the dielectric constant of a vacuum, d_0 is the equilibrium distance between the cation and anion and finally n , the Born parameter, is introduced to account for the compressibility of the ions.

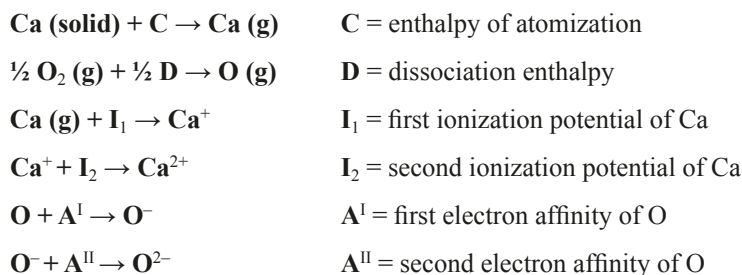
This expression of lattice energy presents the formation of an ionic compound as the binding of ions of opposite sign that approach each other *from infinity* and minimize their energy at the equilibrium distance d_0 . This distance is the point at which the attractive and repulsive forces are balanced. Illustrations of this can be found in any textbook on Inorganic Chemistry.

In the Born-Landé equation, the Madelung constant M plays an important role. M is a geometrical factor that implicitly contains both attractive contributions between ions of opposite sign and repulsive forces between ions of the same sign. *This constant is not characteristic of the compound, but rather of the structure type.* Its value is determined only by the geometry of the lattice and *is independent of the ionic radii and of the ionic charge.* Consequently, the calculation of lattice energy should be limited to simple ionic compounds that have been mentioned. Other structures such as orthosilicates (Mg_2SiO_4), phosphates ($FePO_4$) and silica (SiO_2), that contain strong covalent $X-O$ bonds, need revised electrostatic models. In particular, compounds such as ZnS , will be treated later in this book.

1.3 The Born-Fajans-Haber Cycle

Proving the usefulness of the ionic model in calculating U_{Lat} required the use of a thermodynamic cycle based on experimental standard enthalpies of formation.

Born, Fajans and Haber [3] described this cycle as follows to calculate the lattice energy. Take CaO (NaCl type) as an example of this.



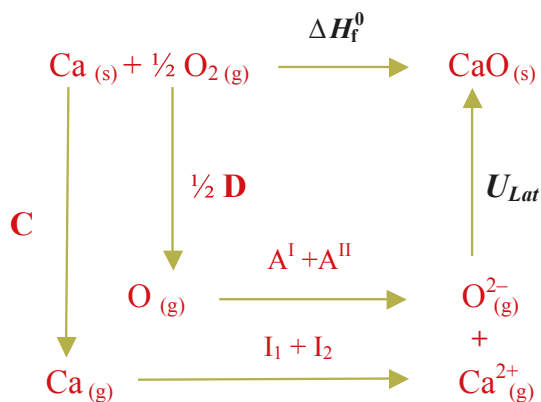
U_{Lat} = Lattice energy released by binding Ca^{2+} and O^{2-} ions approaching each other from infinity up to the equilibrium distance.

ΔH_f^0 = Standard Enthalpy of formation of CaO (solid) from Ca (solid) and O_2 (gas), its elements in their standard states [4].

All these enthalpic processes are integrated in the following expression of the Born-Fajans-Haber cycle (1.2), from which, by applying Hess's law, we can obtain the values of the lattice energy. This process only works when experimental data of the compound's enthalpy of formation are available:

$$\Delta H_f^0 = \text{C} + \text{I}_1 + \text{I}_2 + \frac{1}{2} \text{D} + \text{A}^{\text{I}} + \text{A}^{\text{II}} + U_{\text{Lat}} \quad (1.2)$$

Most of the enthalpies involved in the Born-Fajans-Haber cycle can be estimated experimentally with variable accuracy. For example, measuring the endothermic second electron affinity A^{II} for oxygen is problematic and, therefore, the lattice energy U_{Lat} must be estimated theoretically by means of equation (1.1).



Scheme 1. The Born-Fajans-Haber cycle.

At this point, we must emphasize an important aspect associated with these thermodynamic cycles, i.e. *they could be taken as a mere numbers game* in virtue of the well-known thermodynamic principle saying that every chemical process is only marked by both the initial and the final states.

Thus, since 1917 the ideas of Madelung, Haber and Born, which were based on a predominantly electrostatic model, began to be accepted because of their ability to predict, within reason, the enthalpies of formation of some of those inorganic compounds. The metal atomization process **C**, the energy needed to dissociate molecules **D** together with the mutual ionization of unlike atoms can compel one to think that *the model is founded on electrostatic attractive forces between ions of opposite charge, while the interactions between ions of the same charge, are assigned purely a repulsive character*.

The concept of point charges, that act through the electrostatic interactions, which are used to calculate the Madelung constant **M** and hence U_{Lat} , prompted the recognition of ions and the need of assigning them a size. These ionic sizes, which were considered as *ionic radii*, will be discussed in Chapters 2 and 3.

1.4 The Lack of a Bonding Model for Ionic Compounds

We believe a model that is based on the atomization of metals, followed by their ionization at the infinity, and later ready to be brought together in an “ionized” solid, is intuitive but far from reality. For this reason, attempts to match the calculated U_{Lat} energies with the experimental ones began including covalent contributions, polarizability of ions, etc., leading us to conclude as Waddington [5] that “...*the development of lattice energy is largely an account of the development of the ideas about non-electrostatic forces*”. In this line, Aslanov [6] placed attractive van der Waals forces between anions to justify the values of the lattice energy in compounds with the NaCl- and CsCl-type structures. Interactions between ions of the same sign, in particular anions, have been the subject of recent studies [7] that will be discussed in further chapters.

O’Keeffe [8] after a detailed analysis of many of these aspects, including energetics, bonding, polarizabilities and coordination numbers in ionic solids acknowledges the impossibility of drawing firm conclusions about the validity of the ionic model. He concludes that “when we say that a crystal is *ionic* what is implied is that some simple properties of the crystal are well described by the ionic model”. He notes that “some quantities such as ionic radii or ionicity are sometimes useful concepts but are in principle not determinable”. Some of these aspects will be further considered in Chapters 2 and 3.

The fact that the calculation of the lattice energy had to be done by means of the Born-Fajans-Haber cycle, seems to indicate that the “ionic model”, *rather*

than a bonding model, should be regarded as a “thermodynamic model”, in which every chemical process is marked by the initial $[\text{Ca}_{(s)}]$ and $\text{O}_{2(g)}$ and final $[\text{CaO}_{(s)}]$ states. *Intermediate processes are ideals, serving only as tools to calculate the thermodynamic state functions as the enthalpy of the process.* The enthalpy of atomization \mathbf{C} could be the most significant example of such ideal processes.

QM calculations also provide reliable values of the enthalpy of formation. However, like in the ionic model, these methods also need the information about the structure of the compound. Nevertheless, QM calculations have the advantage of supplying additional “*a posteriori*” information on the bonding nature and other physical properties, data that the ionic model cannot provide.

1.5 The contribution of the Volume Based Thermodynamics

The problem associated with the magnitudes involved in the Born cycle can be prevented if we make use of the so-called Volume-based thermodynamics (VBT) model, recently developed by Jenkins and his co-workers [9]. This model which recognizes a new relationship between the formula unit volume, V_m and thermodynamic quantities such as lattice energy, U_{Lat} and entropy, \mathbf{S} , is a link that serves to furnish us with a previously unappreciated connection between crystal structure data (via unit cell volume, $V_m = V_{cell}/Z$) and thermodynamics.

What makes the VBT model interesting is that the values of ΔH_f^0 can be obtained from the unit cell volumes, making the intricate experimental determination of some magnitudes unnecessary. At the same time, it circumvents conceptual problems like atomization of metal structures, as well as the role of electrostatic forces and the covalency inherent to some atomic groups such as SiO_4 and PO_4 among other. The model requires no structural details whatsoever but only a known volume of the formula unit involved. Its usefulness is that it provides a relative measure of stability in the structures. Numerous papers explain this development in considerable detail [9, 10]. For example, we can highlight its ability to predict the thermodynamic stability of the non-existing Na_2SO_2 and Na_2SeO_2 compounds [11] and how the $(\text{SO}_2)^{2-}$ anion has been detected in solution [12, 13] so, opening the possibility of isolating the salts. This point will be considered in detail in Chapter 18.

1.6 The energy calculated by Quantum Mechanical methods

The above sections present us with a new problem: there is no *bonding model for ionic compounds* that is intimately linked to the uncertainties of the structures. It could be argued that prediction proves unnecessary if hundreds of thousands of structures that have been experimentally determined are available in the databases. However, eventually, all these structures had to be *solved* because they were, first, not *predicted* by the existing models.

The difficulty in predicting inorganic structures contrasts with the greater advances in observing molecular compounds. The latter has been facilitated by the existence of bonding models like the Pauling's Valence Bond model (VB) or in the molecular orbital theory (MO) of Hund, Mulliken, Slater and Lennard-Jones. It is also true that molecular mechanics also helped in determining the molecular conformations.

The energy of any molecule can be obtained by solving the Schrödinger equation that is independent of time [14]:

$$H\Psi = E\Psi \quad (1.3)$$

The wave function of a molecule depends on its conformation and if we know this, we can determine its wave function Ψ and hence calculate its energy.

From this viewpoint, molecular chemistry is closer to prediction and, above all, to explaining the structures than is solid-state chemistry. However, in inorganic solids models based on valence bond or molecular orbital theories, have not served to provide hints for their structural skeletons. Thus, the difficulties in anticipating inorganic structures on the basis of directional bonds has probably prompted the search for predictive methods founded in *ab initio* computations as well as in topological similarities with related compounds. Predicting crystal structures has become one of the most important challenges in solid-state chemistry.

1.7 Can structures be predicted?

That these predictive models do not reliably *predict* structure, even for simple solids, remains a controversy among some. Maddox [15] in particular called this a “scandal in the physical sciences” and Gavezzotti [16] abounds with similar ideas. The reasons for such a failure are partly due to the inverse relationships between order and energy and between the dimensionality and diversity of the plausible crystal structures. The chances that a random search will find the ground state decrease exponentially by increasing the number of atoms involved in the structure.

Even though the challenge remains nowadays, there have been significant advances toward this cause with the increase in computing capabilities and the development of new first-principles QM codes and global searching methods as well. It is not our aim here to make a detailed description of the different methods but just to enumerate briefly the most significant contributions to Crystal Structure Prediction (CSP) in the following section. The reader can find complete summaries of these methods in references [17-19].

1.8 The predictive methods

There are two methods that ought to be distinguished: the structure modelling and the structure prediction. Modelling consists of the minimization of the lattice energy based on interatomic potentials. This technique is now routine work and, when applied to inorganic solids, manages to calculate unit cell parameters within 1%. It should be stressed, however, that *such calculations are not predictions*.

On the contrary, predictions must start from no empirical information on the atomic positions in the unit cell. Moreover, a genuine predictive method should not include the experimentally determined lattice parameters, although less restrictive methods arrive at the unit cell constants with the only input data being the cell contents.

Here we will describe some methods used for Crystal Structure Prediction (CSP):

1. *Random sampling*. - Freeman and Catlow [20] pioneered this method that was followed later by van Eijck and Kroon [21] and by Pickard and Needs (2006) [22, 23]. The method is *no-learning* and works well for small clusters (about 10 atoms). Thus, energy landscapes of $(MX)_{12}$ clusters were obtained for materials with tetrahedral skeletons (wurtzite or sphalerite) such as LiF, BeO, BN, AlN, among others. A similar study was reported on CuF, a much-debated compound in the past century. It was reported that CuF had the sphalerite structure but the synthesis could never be reproduced. Instead, theoretical predictions [24] assign to CuF a cinnabar-like (HgS) structure to CuF.
2. *Simulated annealing*. - The system is *no-learning* and it derives from simple concepts on physical annealing [25-27]. When a molten metal, is slowly cooled, the atoms may crystallize reaching the global minimum. Within the molecular dynamics simulation (Metropolis criterion) the initial temperature is chosen high enough to allow the system to overcome easily energy barriers between local minima. This method has been used to assist in the synthesis planning [27, 28].
3. *Genetic algorithm methods*. - These are “*learning*” procedures, based on evolutionary algorithms acting on a population of structures. They are conceived to avoid the problems associated with a single starting point. The algorithm works by mimicking Darwinian or Lamarckian evolution [29-33]. The code USPEX [34] uses a hybrid evolutionary algorithm.

The use of computational techniques as a tool in structural studies of complex solids is increasingly the standard, and genuine predictions are now being reported for several classes of materials. However, following Woodley and Catlow [17] *structure prediction will continue to challenge our ingenuity for many years to come*.

1.9 The structures remain unexplained

In many instances, CSP is founded in data mining and also in structure similarities with related compounds. See, for example, the predictions of new Li_2S and Na_2S phases [28, 35-37]. The prediction of a new high-pressure phase for nitrogen that reproduces the pseudo-P skeleton of Si^{-1} charged atoms in the SrSi_2 Zintl phase [38] and the possible stabilisation of the Bc8 structure for carbon at pressures of the order of TPa [39]. This structure is formed by Si and Ge at much more lower pressures [40].

So far, we have described aspects concerning the calculation of the lattice energy of compounds, a problem that can be presently afforded by QM and also by means of the VBT methods [9], which enable us to deduce the stability of an unknown compound. In this context, it is pertinent to bring Coulson's ideas to the table involving the two observable facts that a bonding model must account for: the energy and the structure. Reasonable values of ΔH_f^0 and U_{Lat} can be obtained for simple compounds. However, the second main problem, that is the structure, remains unsolved. As we will see in Chapter 2, nobody has been able so far to explain why the structures are as they are or to predict the structure type that a new compound will adopt.

In conclusion, despite the efforts made by solid-state theoreticians after one whole century of X-ray diffraction, the reasons why NaCl , SiO_2 , TiO_2 , ZnO , ZnS , etc. adopt the structures they do remain unknown to us. The hundreds of thousands of structures we know so far had to be determined because they could not be predicted but even if prediction were possible we have their explanations. Prediction and explanation of structures are still a challenge that makes it difficult to hold the "ionic model" as a true bonding model.

Summary

Since the 1920's, inorganic solids, mostly oxides, are thought to be formed by positive cations and negative anions whose structure is stabilized by electrostatic interactions. This model, generally accepted by its capability of predicting both ΔH_f^0 and the lattice energy U_{Lat} by means of the Born-Haber-Fajans cycle, is unable of predicting the structures of the compounds. Because any bonding model should account for both the *energy and the structure* of a given compound, *the ionic model rather than a bonding model is a thermodynamic model*. QM calculations and VolumeBasedThermodynamics also provide reliable values of the energy

but they also need of structural information. Even the Crystal Structure Prediction methods, based on data mining and evolutionary algorithms are unable of doing *ab initio* predictions. However, even if *prediction* were possible, inorganic structures have to be *explained*, a challenge that makes it difficult to hold the “ionic model” as a true bonding model.

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CHAPTER 2

The second basis of the ionic model: Close packed anionic array and the sizes of ions

2.1 The first crystal structures solved: Their influence on the ionic model

The ionic model describes the structures as closest-packed arrays of bulky anions with small cations occupying interstices of that anionic array. As it was discussed in Chapter 1, this descriptive model was derived from concepts like the Madelung constant M and also from experimental results such as the crystal structure determination of NaCl by the Bragg's in 1913 as well as other crystal structures that were solved in following years.

At that time (1916) Lewis and Langmuir published the concept of *covalent bond*, which was defined as a pair of electrons shared by the two bonded atoms, so that each atom completes one octet in its valence shell. Thus, *the sharing of electron pairs and the octet rule* were two of the most fruitful ideas at that time. Although compounds like NaCl, could be thought of as formed by discrete Na-Cl molecules bonded by covalent bonds, the experimental results showed that Na^+ cations and Cl^- anions formed a three-dimensional structure that could be explained through electrostatic attractions.

It is important to bear in mind the structures solved in the early years of the X-ray crystallography, listed in Table 2.1. Some of them (C, Si, Sn and Sb) represented a valuable test to the concept of covalence and the fulfilment of the octet rule. Many others (NaCl , CaF_2 , Fe_3O_4 , MgAl_2O_4 , NiO, NaF, etc.) were regarded as an evidence of the existence of ions that decisively influenced the development of the ionic model. Several of these structures could be described as close-packed anionic arrays in which cations occupied octahedral or tetrahedral voids.

For example, in NaCl, bulky Cl^- anions form a cubic closest packed array, with all the octahedral voids filled with Na^+ cations. In spinel (MgAl_2O_4) a slightly distorted f.c.c.-array of O atoms had $\frac{1}{2}$ of the octahedral holes occupied by the Al^{3+} cations while $\frac{1}{8}$ of the tetrahedral voids were filled with Mg^{2+} cations.

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