

CONTENTS

Preface	xxiii
List of abbreviations	xxvii

CHAPTER 1

The basis of the classic crystal chemistry	1
1.1 Introduction.....	1
1.2 The energy calculation	2
1.3 The Born-Fajans-Haber Cycle	2
1.4 The Lack of a Bonding Model for Ionic Compounds	4
1.5 The contribution of the Volume Based Thermodynamics	5
1.6 The energy calculated by Quantum Mechanical methods	5
1.7 Can structures be predicted?	6
1.8 The predictive methods.....	7
1.9 The structures remain unexplained	8
Summary.....	8
References.....	9

CHAPTER 2

The second basis of the ionic model:	
Close packed anionic array and the sizes of ions	13
2.1 The first crystal structures solved: Their influence on the ionic model....	13
2.2 Two opposite models to explaining the structures: The Goldschmidt-Pauling (GP) model and the Bragg-Slater (BS) model..	14
2.3 The failures of the GP model: Pauling's rules	15
2.4 An alternative to the ionic radii: The extension of Bartell's molecular non-bonded radii to inorganic solids	16
2.5 The atom sizes and the different atomic radii (van der Waals, Non-bonded, Slater-Bragg and Zunger-Cohen)	19
2.6 The attempts to explain the CN as derived from the non-bonded radii ...	21
2.7 Concluding Remarks.....	22
Summary.....	22
References	23

CHAPTER 3

The unsolved challenges of the ionic model	25
3.1 The lack of a general existence of h.c.p. and f.c.c.-arrays	25
3.2 The multiple Coordination Numbers exhibited by cations.....	27

3.3	Interstitial compounds.....	28
3.4	On the atomization of elemental networks	28
3.5	On the existence of ions in crystals	30
3.6	Electron density distribution in metals	33
	Summary.....	35
	References	35

CHAPTER 4

	Searching for alternative models to explain the structures	39
4.1	The reasons for alternative approaches	39
4.2	The discovery of Wondratschek, Merker and Schubert.....	39
4.3	The Lebedev's ideas	40
4.4	Borisov's ideas: Cations in certain structural planes.....	41
4.5	The systematic search of O'Keeffe and Hyde: Oxides as Oxygen-stuffed Alloys	42
4.6	Recognition of metal structures in metal compounds	50
4.7	The constancy of the <i>M-M</i> distances in the oxides	52
4.8	The relation Oxidation-Pressure	54
4.9	The Blatov's contribution: The ToposPro Code and the systematic computational search of structural similarities	60
4.10	Concluding Remarks	61
	Summary.....	62
	References.....	62

CHAPTER 5

	The Zintl-Klemm concept	67
5.1	Introduction.....	67
5.2	What are the Zintl phases?	69
5.3	Description of the structures of some Zintl phases	70
5.4	The structure of Cs ₅ SiP ₃	75
5.5	The bonding in the Zintl phases: Ionic interactions and covalent directed bonds	76
5.6	CaSi and the structure of b.c.c.-Ca	77
5.7	Fullerene-like Zintl polyanions.....	78
	References.....	79
	Summary.....	79

CHAPTER 6

	Cationic arrays and the structures of metals	83
6.1	The structures of metals remain in the oxides.....	83
6.2	The B33 structures as derived from the elemental b.c.c. structures.....	83
6.3	The minerals of the Humite and Leucophoenecite series.....	87
6.4	The puzzling structure of fluoroapatite: Ca ₅ (PO ₄) ₃ F and the structures of elemental calcium.....	91

6.5	The structures of MAl_2O_4 spinels and the structure of f.c.c.-Al	96
6.6	The delafossites $MAIO_2$ (M = Cu, Ag, Au) and the α -NaFeO ₂ -type structures of $M(RE)O_2$ oxides (M = Alkali metal, RE = Rare Earth)	98
6.7	The AlH-substructure of the rutiloide AlOOH	101
6.8	The binary RE oxides.....	102
6.9	The tetragonal phase ($P4/nmm$) of GdO_2 and the structure of Gd	106
6.10	The tetragonal structure of $YbOOH$ and elemental Yb	109
6.11	The structure of rutile TiO_2 and h.c.p.- Ti	110
6.12	From crystal structure data, towards reaction paths in the solid state? ...	112
	Summary	118
	References	119

CHAPTER 7

	The O'Keeffe & Hyde's model revisited: real stuffed alloys	121
7.1	The application of the Oxidation-Pressure concept	121
7.2	New description of the Na_2S and Rb_2S structures	123
7.3	New Description of Li_2S , K_2S and Cs_2S	125
7.4	The M_2SO_4 oxides preserve the structures of the binary M_2S sulfides ..	126
7.5	Extension to other families of structures	134
7.6	Cations are not isolated entities. The AMM concept.....	144
	Summary	146
	References	146

CHAPTER 8

	The structures of "p-Block" elements	151
8.1	Introduction.....	151
8.2	The structures of the Group 14 (Tetrels)	152
8.3	The structures of Group 15 (Pentels)	161
8.4	The structures of Group 16 (Sextels)	165
8.5	Halogens (Heptels).....	168
	References	169
	Summary	169

CHAPTER 9

	The progressive simplification of the structures of the "p-Block"	171
9.1	An introduction.....	171
9.2	The diamond-type structures of C, Si, Ge and Sn	172
9.3	The fragmentation of the dense phases of Si and Ge cl16 ($Ia\bar{3}$): From Si to the HP-HT-Nitrogen structure. Further decomposition into S-helices ...	175
9.4	The decomposition of the C_8 structure: The cubic N_8 molecules, decomposition of the N_8 cube into two S_4 molecules	177
9.5	The dense phase of silicon ($P4_{3}2_1$): Decomposition into tetragonal sulphur helices of HP-Sulfur II.....	178
9.6	The Si-skeleton of Quartz: Decomposition into trigonal Sulphur helices ...	179

9.7	The four-connected network of the PbO-type: Decomposition into the three-connected network of As in As_2O_4 . Further decomposition into tetragonal helices of Sulphur.....	180
9.8	The similarities between the structures of SrAl_2 and SrSi_2	182
9.9	The simple hexagonal structure of Si: Its fragmentation into P_6 molecules	183
9.10	The factual basis of the decomposition mechanisms	184
	Summary.....	185
	References.....	186

CHAPTER 10

	The “<i>p</i>-Block” elements and their oxides	187
10.1	The preservation of the elemental structures in their oxides. An extension of the metal oxides model	187
10.2	The oxides of the Group 14 as derived from the structures of their elements	189
10.3	Structures derived from the Group 4 metals (rutile, $\delta\text{-Ti}_2\text{O}$)	193
10.4	Oxides of the Group 15.....	195
10.5	The Oxides of the Group 16 as derived from the sextels structures	204
	Summary.....	214
	References.....	215

CHAPTER 11

	Why the elemental structures are preserved in their oxides?	217
11.1	The comparable behaviour of bonding pairs and the O atoms.....	217
11.2	On the possible existence of $X\cdots X$ interactions in the $X\text{-O-X}$ groups....	218
11.3	The $X\text{-O-X}$ groups: Angular or Linear?	220
11.4	The $\text{C}9\rightarrow\beta\text{-cristobalite}$ transition: An experimental observation in BPO_4	221
11.5	The Electron Localization Function (ELF) and the Non-Nuclear Maxima (NNM)	224
	Summary.....	228
	References.....	229

CHAPTER 12

	The Zintl-Klemm Concept Extended to the cationic skeletons of oxides: The structures of aluminates	233
12.1	The polyanions of aluminates: Their Al-skeletons as Zintl polyanions...	233
12.2	Nomenclature and Structures	235
12.3	Monoaluminates: Isolated $[\text{AlO}_4]^{5-}$ formal anions	235
12.4	Oligoaluminates	236
12.5	Ring aluminates or cycloaluminates	240
12.6	Chain aluminates.....	241
12.7	Layer aluminates	244
12.8	Tectoaluminates: subdivided according to their connectivity.....	251

12.9 Octahedral versus tetrahedral coordination of Al	257
Summary.....	260
References.....	261

CHAPTER 13**The Zintl-Klemm Concept Extended: The Structures of Silicates (I):
Monosilicates, Oligosilicates, Ring silicates and Chain silicates** 267

13.1 Formula and notation of the Zintl polyanions	267
13.2 Monosilicates	268
13.3 Oligosilicates	268
13.4 Branched oligosilicates	270
13.5 Ring silicates	271
13.6 Double rings or elemental structures of the Group 15?.....	276
13.7 Chain silicates	279
13.8 The structure of sillimanite Al_2SiO_5	287
Summary.....	288
References.....	288

CHAPTER 14**The Zintl-Klemm Concept Extended: Silicates (II).**

Layer silicates and tectosilicates	291
14.1 Layer silicates.....	291
14.2 Single layer silicates: Silicon as Ψ -P	291
14.3 The Ψ - P_2S_3 structure in $\text{La}_3\text{Ga}[\text{Ga}_4\text{SiO}_{14}]$ and the Zintl phase $\text{Yb}_3[\text{Ge}_5\square]$	295
14.4 Double layer silicates: The structure of hexacelsian $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$	299
14.5 Tectosilicates	300
14.6 Underlinked tectosilicates.....	305
14.7 Silicon in octahedral coordination.....	306
14.8 The pyroxene MgSiO_3 at high pressures: The CN does not depend on the ionic radii	309
Summary.....	311
References.....	312

CHAPTER 15**Electronic factors that govern the coordination number** 317

15.1 The linear and the angular geometry of $X-\text{O}-X$ groups in extended solids. Their relationship with isolated molecules.....	317
15.2 Hypervalent molecules.....	318
15.3 Hypervalency in Zintl polyanions: Application to Sb polyanions	320
15.4 The VSEPR model of Gillespie	323
15.5 Hypervalency in the carbocation $[(\text{H}_3\text{C})_3-\text{Si}-\text{CH}_3-\text{Si}-(\text{CH}_3)_3]^+$	326
15.6 The equivalence between the $[(\text{H}_3\text{C})_3-\text{Si}-\text{CH}_3-\text{Si}-(\text{CH}_3)_3]^+$ cation and the Si-O-Si groups.....	328

15.7	The ELF calculations for the $(\text{H}_3\text{C})_3\text{-Si-O-Si-(CH}_3)_3$ molecule	331
15.8	The isoelectronic $(\text{H}_3\text{C})_3\text{-Si-BH}_3\text{-Si-(CH}_3)_3$ molecule	333
15.9	Isolobality and adducts. Its application to the structures of oxides	334
15.10	The structural concordance of P_4 , P_4O_6 , $\text{N}_4(\text{CH}_2)_6$ (hexamethylenetetraamine), $(\text{C}_4\text{H}_4)(\text{CH}_2)_6$ (adamantane) and P_4O_{10}	336
15.11	The decisive example of the molecules of P sulphides: Its extention to the structures of P_4S_3 , $[\text{P}_7]^{3-}$ and nortricyclane	337
15.12	The P sulphides P_4S_3 , P_4S_7 and P_4S_9	339
15.13	Anew discussing about the linearity of the $X\text{-O-X}$ groups	340
	Summary	344
	References	345

CHAPTER 16

Why do atoms occupy the positions they have in the structures?

	Generalization of the Zintl Klemm Concept	351
16.1	Introduction	351
16.2	A new extension of the Zintl-Klemm Concept. The recurrent binary skeletons formed by cations in the oxides.....	352
16.3	The formation of simple alloys structures. The skeletons of the Group 14 elements. The Building Skeletons [BS].....	352
16.4	The structure of Ni_2In revisited. The co-existence of multiple structures.....	354
16.5	The structure of Co_2Si (B8b) and the cotunnite-type structure (PbCl_2)....	358
16.6	The sulphides Na_2S and K_2S and their structural relationship to Co_2Si and Ni_2In . Their multiple substructures	362
16.7	On the need of an electron transfer between cations: sodides, potassides.....	363
16.8	Structures derived from the Novotny-Juza (half-Heusler) phases.....	364
16.9	The structure of eucryptite LiAlSiO_4	367
16.10	The structure of petalite $\text{LiAlSi}_4\text{O}_{10}$	368
16.11	The structure of NaAlSi	369
16.12	The rules governing the Building Skeletons (BS)	370
16.13	The structures of KNaS and CsLiSO_4 as examples of the charge transfer between cations.....	371
16.14	The structure of LiAlSe_2	373
	Summary	374
	References	374

CHAPTER 17

	The simplicity of complex structures	379
17.1	Simple structures underlying in complex atomic arrays.....	379
17.2	Compounds containing atomic groups that are isostructural with CO_3^{2-} ..	379
17.3	The anti-bixbyite structure (Mg_3N_2) and the filled variant (Li_3ScN_2).....	384
17.4	The structures of Ca_3TeO_6 and Cd_3TeO_6	391

17.5 Why is the Extended Zintl-Klemm Concept needed?	393
17.6 New perspectives	395
Summary.....	396
References.....	397
 CHAPTER 18	
Electronic aspects, which justify the structures	401
18.1 Introduction	401
18.2 Application to the Al skeletons in AlX_3 compounds. The AMM (Anions in metallic matrices) Approach.....	402
18.3 New phase transitions in Na and K metals under pressure. The ionization of alkali metals and the localization of electron pairs in $h\text{P}4\text{-Na}$ and $h\text{P}4\text{-K}$	405
18.4 The electron pairs locate at the positions of anions in Na_2S and K_2S . Experimental and theoretical studies. The identical role played by electrons and anions	407
18.5 The valence electrons of Aluminium metal.....	408
18.6 The valence electrons of Calcium metal at high pressure. A comparison with the position of the O atoms in CaO (NaCl and CsCl phases)	409
18.7 The effect of pressure interpreted from ELF calculations	410
18.8 The new Concept of Miao and Hoffmann: Bonding between localized valence electrons. The Interstitial Quasi-atoms Concept (ISQs)	413
18.9 The explanation of a predicted structure: CaC	415
18.10 The stability predictions based on Volume Based Thermodynamics. BVT and Crystallography	417
18.11 Conclusions.....	422
Summary.....	424
References	425
 Formula index.....	 429
Subject index.....	439