

3.60 Symmetry, Structure and Tensor Properties of Materials

IN THIS INTRODUCTORY LECTURE WE WILL USE SOME SIMPLE ELECTROSTATIC PRINCIPLES, WITH WHICH YOU ARE VERY FAMILIAR, PLUS SOME STRAIGHT FORWARD GEOMETRY TO INTRODUCE SOME FUNDAMENTAL FEATURES OF THE CRYSTALLINE STATE — THE APPEARANCE OF SYMMETRY IN LOW-ENERGY STRUCTURES, THE CONCEPT OF PERIODICITY AND A LATTICE AND, FINALLY, SOME SIMPLE GEOMETRY THAT WILL LEAD YOU TO SOME POWERFUL AND NON-INTUITIVE RESULTS FOR THE PREDICTION OF LIKELY STRUCTURES.

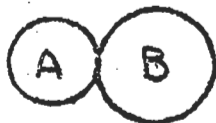
THE LIMITATION ON THESE CONSIDERATIONS IS THAT THE PREDICTIVE POWER IS LIMITED TO IONIC STRUCTURES IN WHICH THE COHESIVE FORCE THAT HOLDS THE ATOMS TOGETHER IS PURELY COULOMBIC. (STRUCTURES HELD TOGETHER BY METALLIC OR COVALENT BONDS ARE MUCH MORE COMPLEX.)

THE FEATURES OF COULOMBIC INTERACTION THAT MAKE THE PRESENT CONSIDERATIONS POSSIBLE IS THAT OUTSIDE THE DISTRIBUTION OF CHARGE ON THE ION THE NET CHARGE MAY BE TREATED AS A POINT AT THE CENTER OF THE ION. THE INTERACTIONS ARE THUS CENTRAL FORCES ACTING THROUGH THE ION CENTERS, AND THE FORCE IS INDEPENDENT OF DIRECTION. A LOW ENERGY STRUCTURE THUS BECOMES A PROBLEM IN EFFICIENT PACKING OF THE IONS

RADIUS RATIO & COORDINATION NUMBER

I. RESTRICTIONS IMPOSED BY THE COORDINATION NUMBER OF ATOM A

$CN_A = 1$



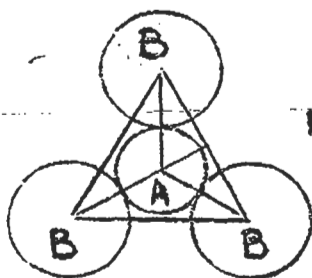
$R_A/R_B = 0 \rightarrow \infty$

$CN_A = 2$



$R_A/R_B = 0 \rightarrow \infty$

$CN_A = 3$

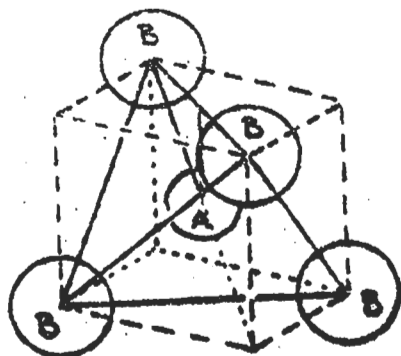


$R_A/R_B = .155 \rightarrow \infty$

$$\frac{R_A + R_B}{R_B} = \frac{2}{\sqrt{3}}$$

$$\frac{R_A}{R_B} = \frac{2}{\sqrt{3}} - 1 = .155$$

$CN_A = 4$



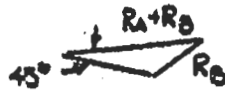
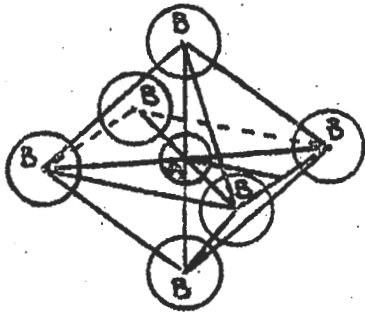
$R_A/R_B = .225 \rightarrow \infty$

$$\frac{R_A + R_B}{R_B} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\frac{R_A}{R_B} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = .225$$

$$CNA = 6$$

$$R_A/R_B = .414 \rightarrow \infty$$

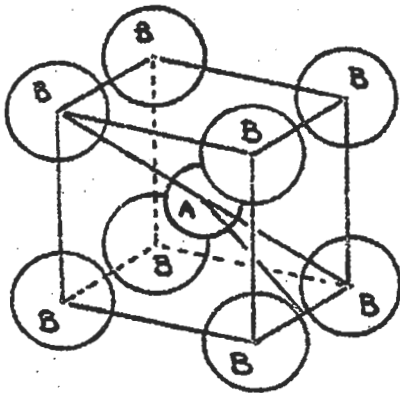


$$\frac{R_A + R_B}{R_B} = \frac{\sqrt{2}}{1}$$

$$R_A/R_B = \sqrt{2} - 1 = .414$$

$$CNA = 8$$

$$R_A/R_B = .732 \rightarrow \infty$$

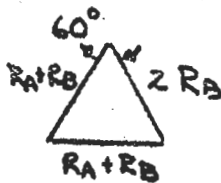
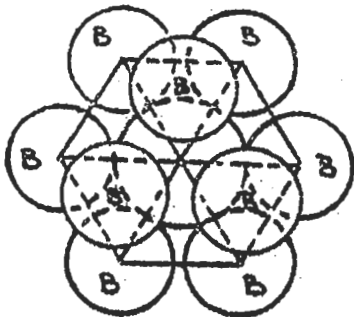


$$\frac{R_A + R_B}{R_B} = \frac{\sqrt{3}}{1}$$

$$R_A/R_B = \sqrt{3} - 1 = .732$$

$$CNA = 12$$

$$R_A/R_B = 1.0 \rightarrow \infty$$



$$\frac{R_A + R_B}{2 R_B} = 1$$

$$R_A/R_B = 2 - 1 = 1.0$$

2. RESTRICTIONS IMPOSED BY THE COORDINATION NUMBER OF ATOM B.

RESULTS ARE THE SAME AS THOSE OBTAINED ABOVE IF WE INTERCHANGE THE LABELING OF THE ATOMS. IF THIS IS DONE, HOWEVER, THE RADIUS RATIO RESTRICTIONS WILL BE IN TERMS OF R_B/R_A . TO EXPRESS ALL RESULTS IN TERMS OF R_A/R_B WE THEREFORE TAKE THE RECIPROALS OF THE NUMBERS OBTAINED ABOVE.

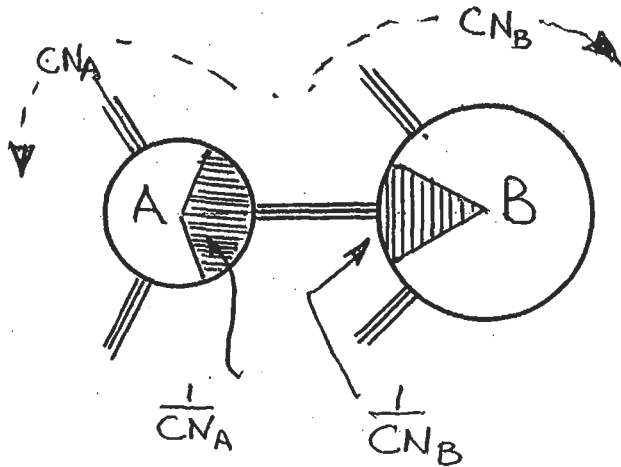
<u>CN_B</u>	<u>R_B/R_A</u>	<u>R_A/R_B</u>
1	$\infty \rightarrow 0$	$1/\infty \rightarrow 1/0 = 0 \rightarrow \infty$
2	$\infty \rightarrow 0$	$1/\infty \rightarrow 1/0 = 0 \rightarrow \infty$
3	$\infty \rightarrow .155$	$1/\infty \rightarrow 1/.155 = 0 \rightarrow 6.45$
4	$\infty \rightarrow .225$	$1/\infty \rightarrow 1/.225 = 0 \rightarrow 4.44$
6	$\infty \rightarrow .414$	$1/\infty \rightarrow 1/.414 = 0 \rightarrow 2.41$
8	$\infty \rightarrow .732$	$1/\infty \rightarrow 1/.732 = 0 \rightarrow 1.37$
12	$\infty \rightarrow 1.0$	$1/\infty \rightarrow 1/1.0 = 0 \rightarrow 1.0$

RELATION BETWEEN COMPOSITION AND COORDINATION

NUMBER

WE WILL CONSIDER VERY SIMPLE BINARY COMPOUNDS IN WHICH

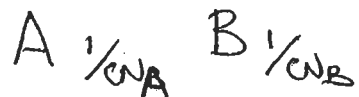
- (1) THERE IS ONLY ONE TYPE OF A ION AND ONE TYPE OF B ION AND
- (2) A IS COORDINATED ONLY BY B AND VICE VERSA



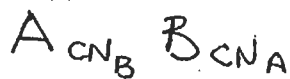
LET A BE SURROUNDED BY A NUMBER OF B NEIGHBORS THAT IS EQUAL TO C_{NA}

LET B BE SURROUNDED BY A NUMBER OF A NEIGHBORS EQUAL TO C_{NB}

IF WE CONSIDER THE BASIC UNIT OF THE STRUCTURE TO BE A "BOND" THEN THE COMPOSITION ASSOCIATED WITH THIS UNIT WILL BE



FRACTIONAL SUBSCRIPTS ON A CHEMICAL FORMULA ARE UGLY — SO LET'S MULTIPLY BY THE INTEGER $C_{NA} \cdot C_{NB}$ TO GET



THEREFORE, SUBJECT TO THE ABOVE ASSUMPTIONS,

IN A COMPOUND OF COMPOSITION $A_m B_n$

THE COORDINATION NUMBERS ARE IN RATIO
 $C_{NA} : C_{NB} = m : n$

3. RESTRICTIONS ON RADIUS RATIO RANGES FOR COMPOUNDS.

FOR ANY COMPOUND $A_n B_m$ THE RATIO OF COORDINATION NUMBERS $CNA/CNB = m/n$. MAKING USE OF THE ABOVE RESULTS:

AB COMPOUNDS

$CNA/CNB = 1:1$	$RA/RB = 0 \rightarrow \infty$	
2:2	$RA/RB = 0 \rightarrow \infty$	
3:3	.155 \rightarrow 6.45	
4:4	.225 \rightarrow 4.44	eg: ZnS
6:6	.414 \rightarrow 2.41	eg: NaCl
8:8	.732 \rightarrow 1.37	eg: CsCl
12:12	1 \rightarrow 1	

AB₂ COMPOUNDS

$CNA/CNB = 2:1$	$RA/RB = 0 \rightarrow \infty$	
4:2	.225 \rightarrow ∞	eg: SiO ₂
6:3	.414 \rightarrow 6.45	eg: TiO ₂
8:4	.732 \rightarrow 4.44	eg: CaF ₂
12:6	1 \rightarrow 2.41	

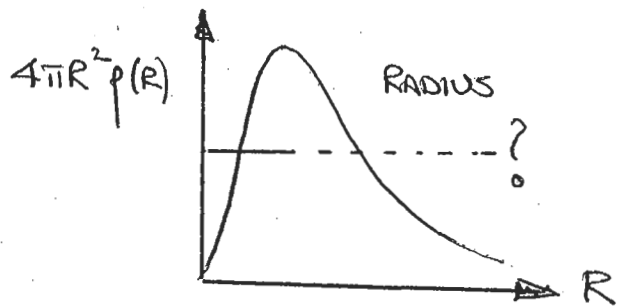
A₂B COMPOUNDS

$CNA:CNB = 1:2$	0 \rightarrow ∞	
2:4	0 \rightarrow 4.44	eg: Cu ₂ O
3:6	.155 \rightarrow 2.41	
4:8	.225 \rightarrow 1.37	eg: Li ₂ O
6:12	.414 \rightarrow 1.0	

A₂B₃ COMPOUNDS

$CNA:CNB = 3:2$.155 \rightarrow ∞	
6:4	.414 \rightarrow 4.44	eg: Al ₂ O ₃
12:8	1 \rightarrow 1.37	

IS THE NOTION OF A "RADIUS" OF AN ION MEANINGFUL?
 NOT REALLY! ATOMS AND IONS ARE FUZZY BALLS OF
 PROBABILITY DENSITY OF THEIR ELECTRONS. THERE ARE SHELLS
 AND LOBES PRESENT THAT ARE SPECIFIED BY THE WAVE FUNCTIONS.



SOMETHING THAT IS ACCESSIBLE
 TO MEASUREMENT BY EXPERIMENT
 ARE INTERATOMIC DISTANCES.
 USING DIFFRACTION TECHNIQUES

ATOMIC POSITIONS IN A CRYSTAL MAY BE MEASURED QUITE
 ACCURATELY — TO ABOUT ONE PART IN 10,000. IF
 THE LOCATIONS OF THE ATOMS ARE FIXED BY SYMMETRY
 THE INTERATOMIC DISTANCES (EG., ONE-HALF OF A CELL EDGE)
 THE INTERATOMIC DISTANCES HAVE THE SAME PRECISION AS THE
 MEASUREMENT OF THE DIMENSIONS OF THE LATTICE. THESE
 MAY BE MEASURED EVEN MORE ACCURATELY; ONE PART
 IN 200,000 OR 0.2×10^{-6} (THERMAL EXPANSION?)

THE INTERIONIC DISTANCE, THEN, MEASURED EXPERIMENTALLY,
 MAY BE TAKEN AS EQUAL TO THE SUM OF THE RADII OF
 THE TWO IONS INVOLVED IN THE INTERACTION.

LET'S SEE HOW WE MIGHT EXTRACT A SYSTEM OF
 RADII, USING THE ALKALI HALIDES AS AN EXAMPLE

$$\text{NaCl} \quad R_{\text{Na}^+} + R_{\text{Cl}^-} = a/2$$

$$\text{KCl} \quad R_{\text{K}^+} + R_{\text{Cl}^-} = a/2$$

$$\text{NaBr} \quad R_{\text{Na}^+} + R_{\text{Br}^-} = a/2$$

⋮

n COMPOUNDS

TWO RADII, ONE DATUM

NOW THREE RADII, TWO DATA

FOUR RADII, THREE DATA

$n+1$ RADII n OBSERVA-
 TIONS

WE CAN'T DO IT!

EXTRACTION OF IONIC RADII FROM SETS OF DATA FOR INTERIONIC DISTANCES

WE CANNOT PERFORM THIS EXERCISE WITHOUT KNOWING THE RADIUS OF AT LEAST ONE SPECIES — WE WILL ALWAYS HAVE ONE MORE UNKNOWN RADIUS THAN EXPERIMENTAL OBSERVATIONS (NOTE THAT HAVING A Cl-Cl DISTANCE AND SETTING R_{Cl} EQUAL TO HALF THE SEPARATION, OR A Na-Na DISTANCE IN ELEMENTAL Na, WON'T WORK! THIS INTERACTION WILL BE A COVALENT OR METALLIC BOND WHICH INVOLVES ATOMIC SEPARATIONS THAT ARE QUITE DIFFERENT THAN THOSE IN AN IONIC BOND!)

EARLY ATTEMPTS TO ESTABLISH AN INITIAL RADIUS

(1) ANION-ANION DISTANCES IN LITHIUM HALIDES (LANDÉ, 1920)

WE ILLUSTRATE THIS APPROACH WITH MORE RECENT DATA FOR SOME COMPOUNDS WITH THE ROCK SALT STRUCTURE

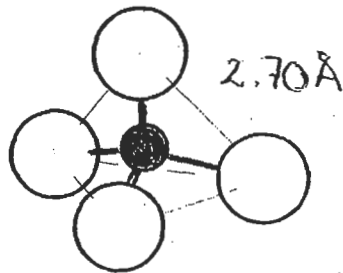
MgO	2.10 Å	MnO	2.24 Å
MgS	2.60	MnS	2.59
MgSe	2.73	MnSe	2.73

FROM THESE DATA WE WOULD SAY THAT THE RADIUS FOR S^{2-} IS 0.50 Å GREATER THAN THAT FOR O^{2-} (WHATEVER THAT MIGHT BE!) AND Se^{2-} IS 0.13 Å GREATER THAN S^{2-} , ALSO Mn^{2+} IS 0.14 Å LARGER THAN Mg^{2+}

THE SAME BUT WHY ARE THE ANION-CATION DISTANCES FOR $MgSe$ AND $MnSe$???!
THE ANIONS MUST BE IN CONTACT!

ATTEMPTS TO ESTABLISH AN INITIAL RADIUS TO PERMIT SEPARATION OF INTERIONIC DISTANCES INTO A SET OF SELF-CONSISTENT IONIC RADII

(b) DIMENSIONS OF THE $\text{Si}_2\text{O}_4^{-4}$ TETRAHEDRON IN SILICATES. EARLY USE OF X-RAYS TO DETERMINE THE ATOMIC ARRANGEMENTS IN SILICATES REVEALED A TIGHTLY-BONDED (CHARGES OF +4 AND -2 AND A SMALL INTERIONIC DISTANCE!) TETRAHEDRON WHOSE SIZE AND SHAPE VARIED VERY LITTLE FROM STRUCTURE TO STRUCTURE



BRAGG (1927) SUGGESTED THAT THIS IS BECAUSE THE STRONG BOND AND SMALL Si^{4+} HAVE PULLED THE OXYGEN IONS INTO CONTACT

THEREFORE, THE RADIUS OF O^{2-} IS 1.35 Å (ACTUALLY, THE $\text{Si}-\text{O}$ BOND IS ONLY ABOUT 50% IONIC. HOWEVER, THIS VALUE IS NOT TOO BAD! — SEE RADIUS TABLES)

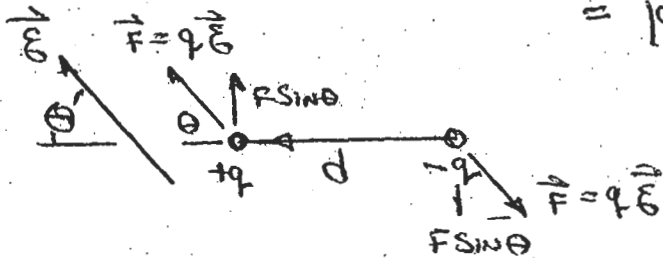
(c) POLARIZABILITY AND INDEX OF REFRACTION

DISCOVERY OF SOME PROPERTY THAT WAS A FUNCTION OF IONIC RADIUS WOULD, IN COMBINATION WITH A SET OF INTERIONIC DISTANCES, WOULD ALLOW ONE TO EXTRACT A SET OF IONIC RADII

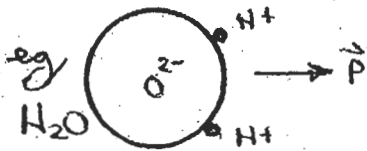
TWO CHARGES $+q$ AND $-q$, EQUAL IN MAGNITUDE BUT OPPOSITE IN SIGN SEPARATED BY A DISTANCE d DEFINE A DIPOLE MOMENT $\vec{P} \equiv qd \vec{J}$.

THERE ARE MANY PROBLEMS IN ELECTROMAGNETISM IN WHICH q , \vec{E} & d APPEAR AS A COMBINED QUANTITY AND, MOREOVER, HAVE A VECTOR QUALITY IF WE DEFINE \vec{d} AS POINTING FROM THE \ominus CHARGE TO THE \oplus CHARGE

FOR EXAMPLE, A DIPOLE MOMENT IN AN ELECTRIC FIELD \vec{E} EXPERIENCES A TORQUE $\tau = |\vec{F}| \sin \theta d = q \vec{E} \sin \theta d = \underline{\underline{\vec{P} \times \vec{E}}}$

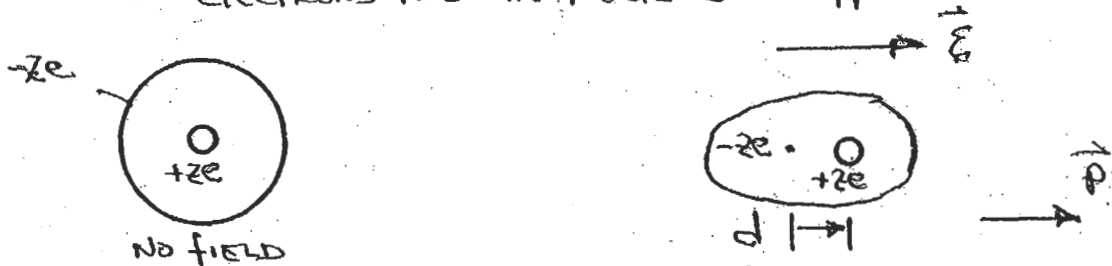


IN ATOMIC SYSTEMS DIPOLE MOMENTS CAN BE EITHER PERMANENT



OR INDUCED AS AN ELECTRIC

FIELD ACTING ON AN ATOM WILL PULL THE ELECTRONS AND THE NUCLEUS IN OPPOSITE DIRECTIONS



LET'S SET UP A VERY SIMPLE MODEL FOR THE DIPOLE MOMENT INDUCED BY THE ACTION OF AN ELECTRIC FIELD, \vec{E} ON AN ATOM, AND SEE WHAT IT PROVIDES.

THE ACTION OF THE FIELD WILL CREATE A DIPOLE MOMENT

$$\vec{P} = Ze d \vec{E}$$

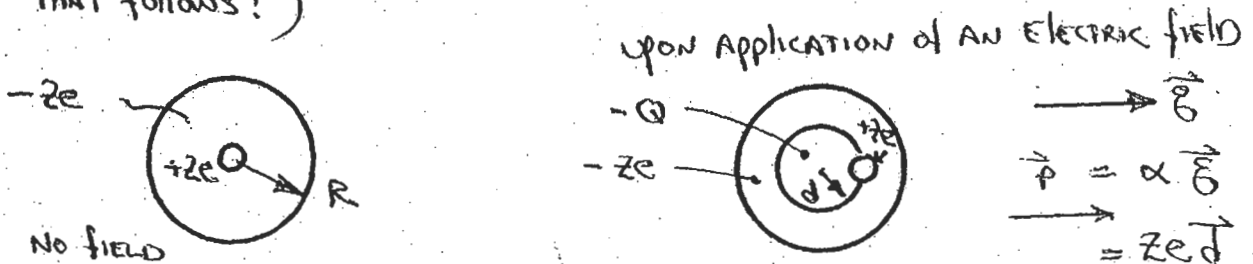
THAT IS PROPORTIONAL TO THE APPLIED ELECTRIC FIELD \vec{E}

$$\vec{P} \propto \vec{E} = \alpha \vec{E}$$

↑ ELECTRONIC POLARIZABILITY

(AN ADVANCE NOTICE OF THINGS TO COME IN THE NEAR FUTURE: \vec{P} IS A VECTOR, \vec{E} IS A VECTOR BUT THERE IS NO REASON WHY \vec{P} MUST BE EXACTLY PARALLEL TO \vec{E} ! THE POLARIZABILITY, THEREFORE, NEED NOT BE A SCALAR NUMBER, BUT INSTEAD, SOMETHING CALLED A TENSOR!)

LET US FURTHER ASSUME THAT THE DENSITY OF ELECTRONS IS UNIFORM (A VERY UNREALISTIC ASSUMPTION!) AND EXTENDS OUT TO A RADIUS R THAT INCLUDES A TOTAL OF Ze CHARGE. WE WILL FURTHER ASSUME THAT THE DISTRIBUTION OF ELECTRONS DISPLACES A DISTANCE \vec{d} RELATIVE TO THE NUCLEUS BUT DOES NOT DEFORM — IT REMAINS A SPHERE OF RADIUS R . (THE REASONS FOR THESE DRASTIC ASSUMPTIONS WILL APPEAR IN THE DEVELOPMENT THAT FOLLOWS!)



THE ELECTRIC FIELD \vec{E} WILL PULL THE NUCLEUS TO THE RIGHT WITH A FORCE $Ze E$ AND PULL THE SPHERE OF ELECTRONS TO THE LEFT WITH A FORCE $-Ze E$. THE CENTER OF THE ELECTRON DISTRIBUTION WILL, THEREFORE, BE DISPLACED BY A DISTANCE d UNTIL THE ATTRACTION BETWEEN THE SPHERE OF ELECTRONS AND THE NUCLEUS JUST BALANCES THE FORCE EXERTED BY THE ELECTRIC FIELD, \vec{E} .

WE NOW EMPLOY TWO RESULTS OF ELECTROMAGNETISM THAT GREATLY SIMPLIFY THIS PROBLEM.

(a) A CHARGE MOVING WITHIN A UNIFORM SHELL OF CHARGE EXPERIENCES ZERO FORCE ANYWHERE WITHIN THAT SHELL

THE RESTORING FORCE THAT BALANCES THE EFFECT OF THE APPLIED FIELD \vec{E} IS THUS THE ATTRACTION BETWEEN THE NUCLEUS, CHARGE Ze AND THE CHARGE Q THAT IS CONTAINED WITHIN

A sphere of radius d ABOUT THE CENTER OF THE SPHERE OF ELECTRONS.

Q IS THUS PROVIDED BY THE RATIO OF THE VOLUME OF THE SPHERE OF RADIUS d , $\frac{4}{3}\pi d^3$, TO THAT OF THE TOTAL VOLUME OF THE DISTRIBUTION OF ELECTRONS $\frac{4}{3}\pi R^3$

$$Q = \frac{\frac{4}{3}\pi d^3}{\frac{4}{3}\pi R^3} \cdot ze = \frac{d^3}{R^3} ze$$

WE NOW EMPLOY TWO FEATURES OF ELECTROMAGNETIC THEORY TO COMPUTE THE DIPOLE MOMENT AND IONIC POLARIZABILITY OF THE ATOM.

(a) ^{A CHARGED PLACED} INSIDE OF A UNIFORMLY-CHARGED SPHERICAL SHELL EXPERIENCES NO FORCE AT ANY POSITION WITHIN THE SHELL.

(b) ELECTROSTATIC FORCE EXERTED BY A DISTRIBUTION OF CHARGE IS THE SAME AS THAT EXERTED BY A POINT CHARGE AT THE CENTER OF THE DISTRIBUTION FOR LOCATIONS OUTSIDE OF THE DISTRIBUTION.

THE FORCE THAT ACTS TO BALANCE THE SEPARATION OF THE NUCLEUS AND SPHERE OF ELECTRONS IS THUS THE FORCE BETWEEN A CHARGE $+ze$ AND CHARGE $-Q$ SEPARATED BY d . EQUATING THIS TO THE FORCE EXERTED BY THE ELECTRIC FIELD E

$$zeE = \frac{1}{4\pi\epsilon_0} \frac{(ze)Q}{d^2} = \frac{1}{4\pi\epsilon_0} \frac{(ze)(ze d^3/R^3)}{d^2}$$

$$E = \frac{(ze)d}{4\pi\epsilon_0 R^3} \quad \text{SO THAT } d = \frac{4\pi\epsilon_0 R^3}{ze} E$$

COMPUTING THE DIPOLE MOMENT

$$P = ze d = ze \cdot \frac{4\pi\epsilon_0 R^3}{ze} E \equiv \alpha E$$

WE NOTE THAT THE DIPOLE MOMENT INDEED TURNS OUT TO BE PROPORTIONAL TO E AND THE ^{ELECTRONIC} POLARIZABILITY α IS

$$\boxed{\alpha = 4\pi\epsilon_0 R^3} \quad \alpha \text{ IS PROPORTIONAL TO THE VOLUME OF THE ATOM!}$$

ELECTRONIC POLARIZABILITY α IS RELATED, IN TURN, TO THE INDEX OF REFRACTION, n , OF A MATERIAL BY THE LORENZ-LORENTZ EQUATION.

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \sum N_i \alpha_i \quad \text{WHERE } N_i \text{ IS THE}$$

NUMBER PER UNIT VOLUME OF SPECIES i OR, IN ANOTHER FORM

$$\frac{M}{\rho} \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} L \alpha$$

WHERE $\left\{ \begin{array}{l} M = \text{MOLEC. WT} \\ \rho = \text{DENSITY} \\ L = \text{AVOGADRO'S NUMBER} \\ \alpha = \text{POLARIZABILITY PER "MOLEWT"} \end{array} \right.$

THE DIELECTRIC CONSTANT, ϵ , OF A MATERIAL IS RELATED TO INDEX OF REFRACTION n BY

$$\epsilon = n^2$$

THE ABOVE RELATIONS MAY, THEREFORE, BE WRITTEN IN TERMS OF ϵ (UPON WHICH THEY BECOME KNOWN AS THE CLAUSIUS-MOSSOTTI EQUATIONS)

A SETS OF ELECTRONIC POLARIZABILITIES FOR IONS HAS BEEN ESTABLISHED FOR A NUMBER OF SPECIES BY TESSMAN, KAHN AND SHOCKLEY (PHYS. REV. 92 890 (1953))

TABLE OF IONIC RADII (A)

G = Goldschmidt
SKR. NORSKE VID. VSK.
NSAR 1, NO. 2 (1926)

P = Pauling
J. AM. CHEM. SOC.
49, 765 (1927)

Z = Zachariasen
Z. KRIST. 80, 137 (1931)

A = Ahrens
Geochim. Cosmochim. Acta 2, 155 (1952)

ION	G	P	A	Z
Ac +3			1.18	1.11
Ag +1	1.13	1.26	1.26	
+2			.89	
Al +3	.57	.50	.51	.45
Am +3			1.07	.99
+4			.92	.89
As +3			.58	
+5		.47	.46	
At +7			.62	
-1				2.27
Au +1		1.37	1.37	
+3			.85	
B +3		.20	.23	.16
Ba +2	1.43	1.35	1.34	1.29
Br +2	.34	.31	.35	.30
Bi +3			.93	
+5		.74	.74	
Br -1	1.96	1.95		1.96
+7			.39	
C +4	.20	.15	.16	.19
Ca +2	1.06	.99	.99	.94
Cd +2	1.03	.97	.97	
Ce +3	1.18		1.07	
+4	1.02	1.01	.94	.92
Cl +7		.26	.27	
-1	1.81	1.81		1.81
Co +2	.82	.92	.73	
+3			.63	
Cr +3	.65		.63	
+6	.34	.52	.52	

For a recent and more extensive compilation see:
 R. D. Shannon & C. T. PreWitt, Acta Crystallographica B25, 925-946 (1969).

ION	G	P	A	Z
Cs +1	1.65	1.69	1.67	1.67
Cu +1		.96	.96	
+2			.72	
Dy +3			.92	
Er +3	1.04		.89	
Eu +3			.98	
F +7			.08	
-1	1.33	1.36		1.33
Fe +2	.83	.75	.74	
+3	.67		.64	
Fz +1		1.75	1.80	1.75
Ga +3	.62	.62	.62	
Gd +3	1.11		.97	
Ge +2			.73	
+4	.53	.44	.53	
Hf +4			.78	
Hg +2	1.12	1.10	1.10	
Ho +3			.91	
I +1			.62	
+7		.50	.50	
-1	2.20	2.16		2.19
In +3	.92	.81	.81	
Ir +4	.66	.64	.68	
K +1	1.33	1.33	1.33	1.33
La +3	1.22	1.15	1.14	1.04
Li +1	.78	.60	.68	.68
Lu +3	.99		.85	
Mg +2	.78	.65	.67	.65

ION	G	P	A	Z
Mn +2	.91	.80	.80	
+3	.52	.50	.66	
+4		.46	.60	
+7			.46	
Mo +4	.68	.66	.69	
+6		.62	.62	
N +3			.16	
+5	.1-.2	.11	.13	.1-.2
NH ₄ ⁺	1.43			
Na +1	.98	.95	.94	.98
Nb +4			.74	
+5			.69	.67
Nd +3			1.04	
Ni +2	.78	.69	.69	
NP +3			1.10	1.01
+4			.95	.92
+7			.71	
O +6			.10	
-2	1.32	1.40		1.46
Os +4	.64	.65	.69	
P +3			.44	
+5	.3-.4	.34	.35	.34
Pa +3			1.13	1.05
+4			.98	.96
+5			.89	.90
Pb +2	1.32	1.21	1.20	
+4	.84	.84	.84	
Pd +2			.80	
+4			.65	
Pm +3			1.06	
Po +6			.64	
Pr +3	1.16		1.06	
Pr +4	1.00	.92	.92	
Pt +2			.80	
+4			.65	
Pu +3			1.08	1.00
+4			.93	.90
Pu +2			1.43	1.37
Pb +1	1.49	1.48	1.47	1.48
Rf +7			.56	
Rh +3	.69		.68	
Ru +4	.65	.63	.67	

ION	G	P	A	Z
S +4			.37	
+6	.34	.29	.30	
-2	1.74	1.84		1.90
Sb +3			.76	
+5		.62	.62	
Sc +3	.83	.81	.81	.68
Se +4			.50	
+6	.3-.4	.42	.42	
-2	1.91	1.98		2.02
Si +4	.39	.41	.42	.38
Sm +3			1.00	
Sn +2			.93	
+4	.74	.71	.71	
Sr +2	1.27	1.13	1.12	1.10
Ta +5			.68	
Tb +3			.93	
+4			.81	
Tc +7			.57	
Te +4	.89	.81	.70	
+6		.56	.56	
-2	2.11	2.21		2.22
Th +4	1.10	1.02	1.02	.99
Ti +3			.76	
+4	.64	.68	.68	.60
Tl +1	1.49	1.44	1.41	
+3	1.05	.95	.95	
Tm +3	1.04		.87	
U +4	1.05	.97	.97	.93
+6			.80	.83
V +2			.95	
+3			.74	
+4	.61	.59	.63	
+5	.4	.59	.59	
W +4	.63	.66	.70	
+6			.62	
Y +3	1.06	.93	.92	.88
Yb +3	1.00		.86	
Zn +2	.83	.74	.74	
Zr +4	.87	.80	.79	.77

Pauling's Rules for Ionic Structures.

(A) A coordination polyhedron of anions is formed about each cation. The cation-anion distance is determined by the sum of their radii. The coordination number is determined by the radius ratio.

(B) Define the "strength" of a cation-anion bond as the ratio of the cation charge to the cation coordination number. In a stable structure the total strength of the bonds that reach an anion in a coordination polyhedron from all neighboring cations is equal to the charge of the anion.

(C) The linkage of coordination polyhedra in a structure is such that edges, and especially faces, tend not to be shared. If edges are shared they tend to be shortened.

(D) Since sharing of polyhedral edges decreases the stability of a structure, cations with high charge and low coordination number especially do not share edges.

(E) The number of different kinds of atoms in a structure tends to be small.

Pauling's Rules for Ionic Structures.

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This Rule has three statements.

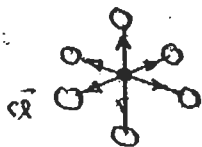
- (a) A coordination polyhedron of anions is formed about each cation (based on the principle that the most stable ionic structure will be one in which the maximum number of anions surround the cation, as the interaction between them is attractive, and vice versa). If a coordination polyhedron of cations is thus formed about the anion as well, why does Pauling mention only the cation coordination polyhedron? The reason is that this is the critical coordination polyhedron that determines the coordination numbers in most ionic structures because the anions are larger than cations.)
- (b) The cation-anion distance is determined by the sum of their radii (well, this is in fact the way we defined the concept of ionic "radii". Two implications of the rule are worth noting. That the distance is is determined by the sum of "radii" affirms that establishment of a self-consistent radii is indeed possible. The second aspect of the statement that is worth noting that we will refer to the arrangement of the large anions in many ionic structures as "close packed". This will indeed be the geometry of their placement but the anions are not in contact. The cation-anion distance being equal to the sum of their radii is what determines the anion-anion distance.)
- (c) Coordination number is determined by radius ratio (if the coordination number becomes sufficiently large that the anions touch we have paid the price of larger repulsion without gaining the ^{full} decrease in energy that results from the cohesive cation-anion interaction.)

(B) Define the "strength" of a cation-anion bond as the ratio of the cation charge to the cation coordination number. In a stable structure the total strength of the bonds that reach an anion in a coordination polyhedron from all neighboring cations is equal to the charge of the anion.

This rule — the only one that is quantitative — is a neat way of formulating the expectation that a stable structure will be electrically neutral on an atomic scale as well as macroscopically. Putting all cations in one corner of a cell and placing all anions in the opposite corner would provide a configuration that was electrically neutral, but hardly an arrangement that is one of low energy.

Let's illustrate the application of this rule for rock salt, NaCl, that is described below. The coordination numbers are

in



Each Na^+ , being surrounded by six Cl^- "donates" a bond of strength

$$S = \frac{+1}{6}$$

Each Cl^- is surrounded by six Na^+

the sum of the bond strengths is thus

$$\sum S = 6 \cdot \frac{1}{6} = 1, \text{ the charge on } \text{Cl}^-$$

This result is almost trivial — and will follow for any AB structure because A and B must, from the composition, have the same charge and the same coordination numbers

The structure of spinel, MgAl_2O_4 , provides a less trivial example as there are two cations present with different charge and coordination number.

The coordination number of Mg^{2+} is 4

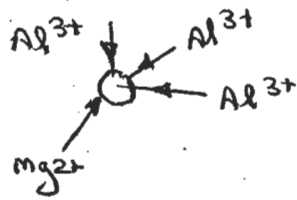
$$S_{\text{Mg}} = \frac{+2}{4} = \frac{1}{2}$$

The coordination number of Al^{3+} is 6

$$S_{\text{Al}} = \frac{+3}{6} = \frac{1}{2}$$

(SPINEL, CONTINUED)

Each O^{2-} ion in the SPINEL structure is surrounded by 3 Al^{3+} with bonds that extend in directions that are parallel to the edges of a cube, plus one Mg^{2+} bond in an orientation that corresponds to the body diagonal of a cube.

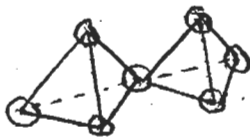


Thus

$$\begin{aligned} \sum S &= S_{Mg} + 3 S_{Al} \\ &= \frac{1}{2} + 3 \frac{1}{2} = 2 \text{ THE} \\ &\text{CHARGE OF } O^{2-} \end{aligned}$$

THE RULE ALSO PERMITS THE PREDICTION OF STRUCTURAL FEATURES THAT ARE FAR FROM OBVIOUS!

THE INVARIABLE (WELL ALMOST—THERE EXIST A SMALL HANDFUL OF HIGH PRESSURE OXIDES IN WHICH Si^{4+} ENTERS AN OCTAHEDRAL SITE!) STRUCTURAL UNIT IN SILICATES IS A TIGHTLY BOUND SiO_4^{-4} TETRAHEDRON. THESE TETRAHEDRA OFTEN LINK BY SHARING OF CORNERS (SEE NEXT TWO RULES)



THE BOND STRENGTH DONATED BY Si^{4+} IS

$$S = \frac{+4}{4} = 1$$

FOR THE O^{2-} AT THE SHARED CORNER

$$\sum S = 2 \times \frac{1}{2} = 2$$

THUS SILICATE STRUCTURES CAN FORM A MIND-BOGGLING ARRAY OF STRUCTURES CONTAINING RINGS, CHAINS, SHEETS OR NETWORKS OF TETRAHEDRA BUT ONLY TWO TETRAHEDRA CAN SHARE A CORNER

PHOSPHATE STRUCTURES $P^{5+}O_4^{-3}$ (THE P-O BOND, HOWEVER, HAS CONSIDERABLE COVALENT CHARACTER) WOULD HAVE

$$S = \frac{+5}{4} = 1\frac{1}{4} \text{ THEREFORE } PO_4 \text{ TETRAHEDRA}$$

CANNOT SHARE CORNERS, MUST BE ISOLATED IN PHOSPHATES

Al^{3+} SOMETIMES HAS TETRAHEDRAL COORDINATION BY OXYGEN

BUT $S_{AP} = \frac{+3}{4}$ THUS 4 THE TETRAHEDRA SHARE
CORNERS, THAT OXYGEN ION MUST ALSO BE BONDED TO SOME
ADDITIONAL CATION

LET'S, IN CONCLUSION, CONSIDER THE PHASE $AlPO_4$. THIS
COMPOSITION CAN FORM A NETWORK OF CORNER SHARING TETRAHEDRA
IF THE Al^{3+} AND P^{5+} POLYHEDRA ALTERNATE!



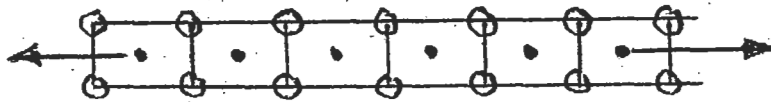
$$\begin{aligned}\sum S &= S_{AP} + S_P \\ &= \frac{3}{4} + \frac{5}{4} = 2\end{aligned}$$

$AlPO_4$, IT TURNS OUT, HAS STRUCTURES (THERE ARE SEVERAL) THAT
ARE EXACTLY THE SAME AS THOSE OF SiO_2 !!

(C) The linkage of coordination polyhedra in a structure is such that edges, and especially faces, tend not to be shared. If edges are shared they tend to be shortened.

The basis for this rule is that, regardless of coordination number, the cations inside of the polyhedra get progressively closer as the polyhedra share corners, edges and faces.

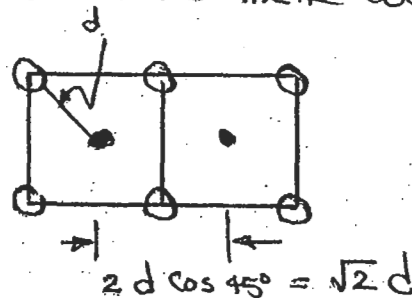
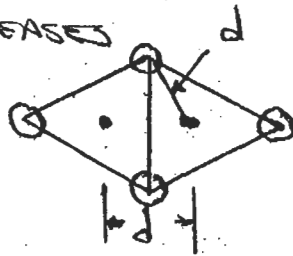
The origin of the observation in the second part of the rule is that repulsion between the cations in a chain of edge-shared polyhedra will expand, accordion-style.



The same thing (for similar reasons) will occur for the edges of a shared face (relative to the unshared edges) for a string of face-shared polyhedra.

(D) Since sharing of polyhedral edges decreases the stability of a structure, cations with high charge and low coordination number especially do not share edges.

The origin of this observation is that (bond-distance remaining constant) the distance between the cations inside of the polyhedra rapidly decreases as their coordination number decreases.



(2). The number of different kinds of atoms in a structure tends to be small.

THIS RULE — SOMETIMES REFERRED TO AS "THE LAW OF PARSIMONY" — CAN BE INTERPRETED FOR TWO MEANINGS OF "DIFFERENT": DIFFERENT STRUCTURALLY OR DIFFERENT CHEMICALLY. IN THE STRUCTURE ASSUMED BY A GIVEN COMPOUND ONE WOULD NOT EXPECT A GIVEN SPECIES TO BE PRESENT WITH MANY DIFFERENT COORDINATION NUMBERS. THE STRUCTURES WOULD NOT HAVE LOW ENERGY BECAUSE IT WOULD JUST BE TOO DIFFICULT TO FIT TOGETHER EFFICIENTLY.

THE "CHEMICAL" DIFFERENCE INTERPRETATION WOULD SUGGEST THAT, IF ONE MELTED TOGETHER IN A POT ALL OF THE ATOMS IN THE PERIODIC TABLE, ONE WOULD NOT EXPECT THEM TO CRYSTALLIZE INTO A SINGLE STRUCTURE. THE COST OF ENERGY TO DO THIS FOR IONS OF DIFFERENT SIZE, WITH DIFFERENT COORDINATION NUMBERS AS WELL, WOULD SIMPLY BE TOO GREAT. IT WOULD BE MORE EFFICIENT TO PARTITION THE CHEMICAL SPECIES INTO DIFFERENT STRUCTURES AND PAY THE PRICE, IN ENERGY, TO FOR THE INTERFACE BETWEEN THEM.