Atomic and Ionic Sizes

Any definition of atomic or ionic size is inexact because the electron density of an atom or ion decays exponentially away from the nucleus. Nevertheless, every given pair of atoms typically shows a narrow range of internuclear distances in chemical structures where they occur. The primary factors influencing these interatomic distances are repulsive forces between electrons and electron pairs and attractive forces between valence electrons and nuclei. As a result, various sets of atomic and ionic radii have been constructed, and this information is useful for solving or assessing new chemical structures, especially when they are complex.

READING: A.F. Wells, *Structural Inorganic Chemistry*, 5th Ed., pp. 287-291, 312-321, 1286-1295; J.K. Burdett, *Chemical Bonding in Solids*, pp. 191-207.

(33) *Radii Scales*: Nearly all atomic and ionic radii are derived from empirical and statistical analyses of extensive surveys of known compounds and interatomic distances,[31] but radii have also been computed using quantum chemical approaches.[32] To place radii on the same scale or the same perspective, the values should be corrected for certain characteristics such as coordination numbers, valence states of atoms in covalent bonds, e.g., sp, sp^2, or sp^3 hybridization, and formal oxidation states in ionic or polar bonds. Important examples of atomic or ionic radii scales include:

- *Slater radii* are "… empirical atomic radii…, such that the sum of the radii of two atoms forming a bond in a crystal or molecule gives an approximate value of the internuclear distance. They hold for covalent, metallic, and ionic binding equally well." [33]
- *Pauling radii* distinguish atomic sizes by covalent,[34] ionic,[35] and metallic[36] substances.
- *Shannon* and *Prewitt* crystal radii,[37] are essentially ionic radii that cover a wide range of oxidation states and coordination environments for every element.

The values of atomic and ionic radii follow certain periodic trends:

(i) Radii *increase* going down a group from lightest to heaviest elements due to electronic repulsions between core and valence electrons. Various radii of the 4*d* and 5*d* metals are exceptions to this trend because electrons in the 4*f* subshell do not shield valence 5*d* electrons effectively from their nuclei. As a result, the 5*d* electrons experience exceptionally large effective nuclear charges leading to smaller radii than may be expected for these elements. This effect is called the "lanthanide contraction".

(ii) Radii tend to *decrease* going left-to-right across a period, arising from the general increase in effective nuclear charge on the valence electrons. However, bonding factors can lead to some increasing values, especially near the end of the *d*-series elements in each period.

(iii) Radii *decrease* for a given element as its oxidation state increases. This outcome is a result of electron-electron repulsions and effective nuclear charges on the valence electrons.

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[31] B. Cordero, V. Gómez, A.E. Platero-Prats, M. Revés, J. Echeverria, E. Cremades, F. Barrragán, S. Alvarez, *Dalton Trans.* **2008**, *21*, 2832-2838.
[32] E. Clementi, D.L. Raimondi, W.P. Reinhardt, *J. Chem. Phys.* **1967**, *47*, 1300-1307.
[33] J.C. Slater, *J. Chem. Phys.* **1964**, *41*, 3199-3204.
[34] L. Pauling, M.L. Huggins, *Z. Kristallogr. Cryst. Mater.* **1934**, *87*, 205-238.
[35] L. Pauling, *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, NY: **1960**, Ch. 13.
[36] L. Pauling, *J. Am. Chem. Soc.* **1947**, *69*, 542-553.
[37] R.D. Shannon, *Acta Cryst. Sect. A* **1976**, *A32*, 751-767; R.D. Shannon, C.T. Prewitt, *Acta Cryst. Sect. B* **1969**, *B25*, 925-946.

(iv) Radii *increase* for a given element as its local coordination number increases, because atoms occupy larger volumes as they are surrounded by more ligands. Increasing the number of ligand-ligand repulsions tends to expand the volume accessible to the coordinated atom.

(34) *Metallic radii*, designated as R_{CN}, have been worked out by Pauling and Goldschmidt and are usually defined for the coordination number (CN) 12, i.e., R_{12}, which occurs for HCP and CCP metals. In CCP metals, all 12 nearest neighbor distances are equal, but this is not necessarily the case for HCP metals. Therefore, the metallic radii R_{12} for distorted close packed metals like Zn, Cd, and In, are based on the *averaged* nearest neighbor distance. However, not all metallic elements adopt close packed, 12-coordinate structures. For example, Nb, Mo, Ta, and W are BCC metals, in which each atom has 8 nearest neighbors and 6 second nearest neighbors. Therefore, metallic radii for BCC metals are designated R_8.

For metallic elements adopting non-close packed structures, Goldschmidt derived correction factors α that relate the expected R_{12} value to the observed R_{CN} ($R_{12} = \alpha R_{\text{CN}}$) by assuming that the atomic volume remains fixed between the hypothetical 12-coordinate and the observed structures. In this approach, atomic volume is defined as the volume of the unit cell divided by the number of atoms in the cell such that all space is partitioned to the atoms, i.e., there is no void space. The observed R_{CN}, though, is evaluated using interatomic distances. As an example of this estimation strategy, let's evaluate R_{12} for a BCC metal like Nb (a_{BCC} = 3.300 Å). In BCC sphere packing, the radius R_8 is determined by atomic spheres touching along the unit cell body-diagonals: $4R_8 = \sqrt{3}a_{\text{BCC}}$. The expected value of R_{12} may be determined by using CCP = FCC as the model structure in which atomic spheres touch along the face-diagonals of the cubic cell: $4R_{12} = \sqrt{2}a_{\text{FCC}}$. The Goldschmidt constraint is

$$V_{\text{atom}} = \frac{V_{\text{BCC}}}{2} = \frac{a_{\text{BCC}}{}^3}{2} = \frac{V_{\text{FCC}}}{4} = \frac{a_{\text{FCC}}{}^3}{2},$$

because the BCC cell contains two spheres and the CCP cell contains four spheres. Inserting the relationships for R_8 and R_{12}, respectively, in place of a_{BCC} and a_{FCC} into the Goldschmidt constraint for atomic volumes leads to the result

$$R_{12} = \left(2^{5/6}/3^{1/2}\right)R_8 = 1.029\, R_8,$$

so that the 12-coordinate metallic radius is about 3% larger than the 8-coordinate metallic radius. For Nb, R_8 = 1.429 Å as determined from experimental data, so that R_{12} = 1.470 Å.

Metallic radii are also useful for certain semimetallic and semiconducting main group elements because they are components of close packed intermetallic structures. However, the structures of these elements, Si (4), Ge (4), Sn (4), As (3+3), Sb (3+3), Bi (3+3), Se (2+4), and Te (2+4), have low coordination numbers (noted in parentheses). Using the Goldschmidt approach to estimate R_{12} for these main group elements from their structures is often misleading because they are not densely packed and bonding forces are much more anisotropic than in typical close packed metals. Nevertheless, there are two other ways to estimate the metallic radii R_{12} for these elements:

(1) Use intermetallic compounds with specific chemical compositions and close packed structures to estimate these radii by taking sums of atomic volumes. For example, Cu_3Ge and Ag_3Sb are both HCP-type structures that can provide estimates for R_{12}(Ge) and R_{12}(Sb), respectively. However, because interatomic interactions in intermetallic compounds include some covalency and ionicity, estimations of R_{12} from a single compound or family of compounds are usually of limited value.

(2) Extrapolate the lattice parameters of solid solutions formed by these elements in close packed metals by assuming a linear relation between unit cell parameters and solute concentrations (Vegard's law). However, as a solute, the element is the minority component of the solution with concentrations less than 50 atomic percent, whereas the extrapolation extends to 100% "solute". Also, the relationships between cell parameters and solute concentrations in solid solutions are not always linear and the sizes of solute atoms can be affected by the nature of the solvent atoms.

PROBLEM: Evaluate R_{12}(Ge) using the intermetallic compound Cu_3Ge, which is HCP-like with 6 Cu and 2 Ge atoms per unit cell with and a room temperature volume of 101.464 Å^3. Cu(*s*) is CCP with a room temperature unit cell constant of 3.615 Å.

The packing efficiency of ideal HCP sphere packing is 74.05%, so that the average atomic volume is

$6\ V(\text{Cu}) + 2\ V(\text{Ge}) = (0.7405)(101.464\ \text{Å}^3) = 75.1341\ \text{Å}^3$.

The atomic volume and R_{12} for CCP Cu are

$V(\text{Cu}) = (0.7405)(3.615\ \text{Å})^3 / 4 = 8.746\ \text{Å}^3$ and

$R_{12}(\text{Cu}) = [(3/4\pi)(8.746\ \text{Å}^3)]^{1/3} = 1.278\ \text{Å}$.

Therefore, using these expressions, V(Ge) and R_{12} for Ge in Cu_3Ge can be estimated as

$V(\text{Ge}) = [75.1341\ \text{Å}^3 - 6(8.746\ \text{Å}^3)] / 2 = 11.330\ \text{Å}^3$, and

$R_{12}(\text{Ge}) \sim [(3/4\pi)(11.330\ \text{Å}^3)]^{1/3} = 1.393\ \text{Å}$.

Therefore, R_{12}(Ge) is ~9% larger than R_{12}(Cu). Using these radii, the estimated Cu–Ge distance in Cu_3Ge is 1.278 Å + 1.393 Å = 2.671 Å, which is somewhat longer the experimental values of 2.339 Å, 2.604 Å, 2.655 Å, and 2.639 Å.[38]

(35) The metallic radii of the 4th-6th period elements as a function of group number steadily decrease until around groups 8-9 (Fe, Ru, Os; Co, Rh, Ir), then gradually rise until group 13 (Ga, In, Tl). As expected, 4th period metals are smaller than 5th and 6th period metals (an exception is Mn). Also, beginning at group 4 (Ti, Zr, Hf), the metallic radii for 5th and 6th period metals are very similar, an effect arising from the lanthanide contraction. The reason for the observed trend in 12-coordinate metallic radii is twofold:

(i) Increasing *effective nuclear charge* as group number increases across a period, and

(ii) The *cohesive energy*, which is the energy needed to break a solid into its gaseous atoms, is lowest for groups 1 and 12 and highest for groups 5-6 (V, Nb, Ta; Cr, Mo, W).

Trends in cohesive energies within a period can be understood by a simple energy band model. When metal atoms condense to a solid, the discrete atomic states broaden into energy bands. For the solid, *d*-states lower in energy than those of the free atom are metal-metal *bonding*, and *d*-states higher in energy than those of the free atom are metal-metal *antibonding*. On moving left-to-right across a period, this energy band gets increasingly populated with valence electrons. Filling bonding states increases the cohesive energy by enhancing attractive interatomic forces that bring atoms closer together. As antibonding states are occupied, the interatomic forces become increasingly repulsive, thereby lowering the cohesive energy and increasing the interatomic distances. From cohesive energy arguments alone, the smallest radii for any period of elements should occur for group 5-6 elements, where the energy band would be about half-filled. But, as the effective nuclear charge increases left-to-right across a period, atoms tend to become smaller

[38] E. Caspi, H. Shaked, H. Pinto, M. Melamud, Z. Hu, O. Chmaissem, S. Short, J.D. Jorgensen, *J. Alloys Cmpd.* **1998**, *271*, 378-381.

as the valence electrons feel stronger attractions to their nuclei. Thus, the smallest metallic radii occur for groups 8-9 in each period because occupation of weakly antibonding states for elements just beyond groups 5-6 do not yet disrupt the influence of effective nuclear charges.

(36) *Covalent radii* $R_A(n)$ (A = element; n = covalent bond order) were assigned primarily by Linus Pauling to reflect atomic sizes in covalent bonds.[34] Although these radii vary with bond orders as determined from Lewis structures, the general trend among main group elements is for covalent radii to increase down a group and decrease across a period. Closer examination of the trends of single-bond radii $R_A(1)$ for each group reveals that the 2nd period elements are *unusually small* when compared to their heavier group analogues. To rationalize this observation, *pseudopotentials* are useful because they describe the potentials felt by outer valence electrons in atoms arising from the nucleus and core electrons. The pseudopotential for an atom consists of the valence electron-nuclear attraction, which is screened by the presence of the core electrons, and the valence electron-core electron repulsion, which includes a Pauli-type exchange repulsion associated with two electrons having the same subshell quantum number l. A comparison of the pseudopotentials for C and Si reveals that the 3*p* electrons in Si experience enhanced repulsions from the 2*p* core electrons, whereas the 2*p* electrons in C do not feel corresponding repulsions because there are no "1*p*" electrons. As a result, the 2*p* valence electrons of C experience a larger effective nuclear charge than the 3*p* valence electrons in Si. The corresponding valence *p* electrons of Ge (4*p*), Sn (5*p*), and Pb (6*p*), like the 3*p* valence electrons of Si, also experience enhanced Pauli-type repulsions. Therefore, the covalent radius of the C atom is significantly smaller than the value expected from a linear correlation of the covalent radii of Si, Ge, Sn, and Pb. Similar behavior is observed for the 2*p* elements B, N, O, and F as compared to their heavier group analogues. Likewise, the radii of the second and third period alkali and alkaline-earth metal atoms are smaller than expected from the radii for the fourth, fifth, and sixth period elements because there are no filled "1*d*" or "2*d*" subshells. Smaller covalent radii are expressed in chemical structures as shorter interatomic distances, which lead to larger orbital overlaps, so that 2nd period elements C, N, and O show enhanced π-bonding relative to σ-bonding.

(37) After examining numerous interatomic distances determined by various diffraction and spectroscopic experiments, Pauling proposed the following logarithmic relationship between the distance of an A−A single bond $d_{AA}(1)$ and the distance of an A−A bond with bond order n:

$$d_{AA}(n) - d_{AA}(1) = -0.6 \log n,$$

in which the bond order n is a measure of the covalent bond strength. This relationship can be converted to one between covalent radii if $d_{AA}(n) \sim 2R_A(n)$. Then,

$$R_A(n) = R_A(1) - 0.3 \log n.$$

The value $d_{AA}(n)$ is determined by experiment whereas $d_{AA}(1)$ is a constant evaluated by statistical analyses of numerous structures containing A–A bonds. By rearranging Pauling's expression, the bond order n decreases exponentially with increasing bond distance:

$$n = 10^{[d_{AA}(1) - d_{AA}(n)/0.6]} = \left(10^{d_{AA}(1)/0.6}\right)10^{-d_{AA}(n)/0.6}.$$

This trend in bond order mimics the spatial variation of valence electron density from an atomic nucleus at distances corresponding to observed bond distances.

Pauling also called the bonding power of an atom or ion its *valence*, which is given by either the number of electrons taking part in covalent bonds or as the charge of the ion for ionic bonds. For example, Na, F, and Cu(I) are monovalent (valence = 1); Mg, O, and Co(II) are divalent (valence = 2); Si and Ti(IV) are tetravalent (valence = 4). According to Pauling's notions, an atom's valence can be distributed among the individual bonds formed by the atom, called its *bond valence*, so that the sum of bond valences at an atom equals its atomic valence.

I.D. Brown generalized Pauling's ideas to create the *Bond-Valence Method* as a means to use relative atomic sizes via measured interatomic distances in crystals to analyze complex structures of inorganic compounds.[39] In a chemical compound containing elements A and X, each interatomic A–X contact $d_{AX}(s_{AX})$ is assigned a bond valence s_{AX}, which is evaluated as

$$s_{AX} = e^{[d_{AX}(1) - d_{AX}(s_{AX})/B]},$$

in which $d_{AX}(1)$ and B are empirical parameters for the A–X contact and are determined by fitting data from experimental crystal structures. In more recent developments, the B parameter is typically set at 0.37 Å for all bond pairs. There are tables of parameters $d_{AX}(1)$ for several different bond types A−X with the most extensive compilations assembled for oxides and halides.[40] When using the Bond-Valence Method to analyze structures, there are two fundamental rules:

(a) Valence Sum Rule: Sum of bond valences (s_{AX}) at each atom A = atomic valence at A.

PROCEDURE: For each different atom A in the asymmetric unit, evaluate s_{AX} for every A–X contact and add these values. Their sum equals the atomic valence assigned to A as defined by Pauling.

(b) Rule of Stoichiometry: Total atomic valence of Lewis acids (cations) = total atomic valence of Lewis bases (anions).

PROCEDURE: This rule is simply a check on the calculations of atomic valences. The sum of atomic valences for every "cation" should equal the sum of atomic valences for every "anion".

These rules, along with a few more geometrical ones, were enunciated by Pauling to identify the factors that control structures of "ionic" and "covalent" compounds (see Burdett, pp. 191-218).

(38) The Bond-Valence Method has three useful applications:

(a) To verify or properly formulate chemical structures by examining experimental structures for accuracy, by determining oxidation states for controversial cases, or by identifying bonding instabilities;

(b) To locate light atoms, especially H atoms, that may be especially difficult to find by X-ray diffraction; and

(c) To predict bond distances in potentially new compounds as an alternative to using radii.

We will demonstrate how this approach is applied to formulate a chemical structure (a) and to locate H atoms in a mineral (b):

PROBLEM 1: Transition metals can adopt different oxidation states, which can significantly influence chemical, electrical, and magnetic properties. Devise a formulation of the mineral ilmenite $FeTiO_3$ from its crystal structure using common oxidation states for Fe and Ti.

To apply the Bond-Valence Method, we need the Fe–O and Ti–O distances, which are obtained from the crystal structure of ilmenite: space group $R\overline{3}$; unit cell parameters a = 5.0884 Å and c = 14.0855 Å; and the asymmetric unit consisting of Fe at 6*c* (0, 0, 0.3554), Ti at 6*c* (0, 0, 0.1464), and O at 18*f* (0.3492, 0.0392, 0.0883)). The structure may be described as HCP O atoms with Fe and Ti occupying octahedral voids in alternate layers along ***c***. There are 6 Fe–O contacts per Fe (3× 2.07 Å; 3× 2.20 Å) and 6 Ti–O contacts per Ti (3× 1.88 Å; 3× 2.09 Å).

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[39] (a) I.D. Brown, *Chem. Soc. Rev.* **1978**, *7*, 359-376; (b) I.D Brown, *Structure and Bonding in Crystals*, Vol. II, Academic Press, **1981**, Ch. 14; (c) I.D. Brown, *Chem. Rev.* **2009**, *109*, 6858-6919.

[40] (a) I.D. Brown, D. Altermatt, *Acta Cryst.* **1985**, *B41*, 244-247; (b) M. O'Keeffe, *Acta Cryst.* **1990**, *A46*, 138-142; (c) N. Brese, M. O'Keeffe, *Acta Cryst.* **1991**, *B47*, 192-197.

There are two reasonable formulations of ilmenite: $Fe^{II}Ti^{IV}O_3$ with d^6 Fe^{II} and d^0 Ti^{IV} ; and $Fe^{III}Ti^{III}O_3$ with d^5 Fe^{III} and d^1 Ti^{III}. In the first case, both cations have even numbers of valence electrons and could show diamagnetic behavior. In the second case, unpaired electrons may be expected unless there is significant metal-metal bonding.

Now, calculate the atomic valences for each formulation and assess how they compare to the specific model used. For calculations of bond valences, use B = 0.37 Å:

$Fe^{II}Ti^{IV}O_3$:

Bond-valence parameters are Fe(II)–O, $d(1)$ = 1.734 Å, Ti(IV)–O, $d(1)$ = 1.815 Å.

$s_{FeO}(2.07\ Å) = e^{[(1.734\ Å - 2.07\ Å)/0.37\ Å]} = e^{(-0.908)} = 0.403$
$s_{FeO}(2.20\ Å) = e^{[(1.734\ Å - 2.20\ Å)/0.37\ Å]} = e^{(-1.259)} = 0.283$

$s_{TiO}(1.88\ Å) = e^{[(1.815\ Å - 1.88\ Å)/0.37\ Å]} = e^{(-0.176)} = 0.839$
$s_{TiO}(2.09\ Å) = e^{[(1.815\ Å - 2.09\ Å)/0.37\ Å]} = e^{(-0.743)} = 0.476$

Use these bond valences to evaluate atomic valences:

Fe(II): 3(0.403) + 3(0.283) = 2.058
Ti(IV): 3(0.839) + 3(0.476) = 3.945
O: 0.403 + 0.283 + 0.839 + 0.476 = 2.001

Analysis: the calculated atomic valences agree very well with the model assignments, divalent Fe and tetravalent Ti. The atomic valence of O is very close to 2.

$Fe^{III}Ti^{III}O_3$:

Bond-valence parameters are Fe(III)–O, $d(1)$ = 1.759 Å, Ti(III)–O, $d(1)$ = 1.791 Å.

$s_{FeO}(2.07\ Å) = e^{[(1.759\ Å - 2.07\ Å)/0.37\ Å]} = e^{(-0.841)} = 0.431$
$s_{FeO}(2.20\ Å) = e^{[(1.759\ Å - 2.20\ Å)/0.37\ Å]} = e^{(-1.192)} = 0.304$

$s_{TiO}(1.88\ Å) = e^{[(1.791\ Å - 1.88\ Å)/0.37\ Å]} = e^{(-0.241)} = 0.786$
$s_{TiO}(2.09\ Å) = e^{[(1.791\ Å - 2.09\ Å)/0.37\ Å]} = e^{(-0.808)} = 0.446$

Use these bond valences to evaluate atomic valences:

Fe(III): 3(0.431) + 3(0.304) = 2.205
Ti(III): 3(0.786) + 3(0.446) = 3.696
O: 0.431 + 0.304 + 0.786 + 0.446 = 1.967

Analysis: the calculated atomic valences agree somewhat with the model assignments, trivalent Fe and trivalent Ti, but less well than the alternative formulation. The atomic valence of O is close to 2.

A comparison of these results gives better overall agreement for atomic valences of $Fe^{II}Ti^{IV}O_3$ rather than $Fe^{III}Ti^{III}O_3$. Consistent with this conclusion, ilmenite is diamagnetic.

(39) PROBLEM 2: Locating H atoms can be especially challenging using X-ray diffraction because the scattering power of a one-electron H atom is low as compared to other many-electron atoms. Using deuterated samples, neutron diffraction can effectively locate D(H)-atom positions, but this approach requires a large amount of material and must be conducted at a large facility where neutron beams are generated. The crystal structure of the mineral diaspore AlO(OH) reveals two distinct O atom sites. However, results of X-ray diffraction are unable to unequivocally locate the H atoms and thereby cannot identify which O site is hydroxide. Use the Bond-Valence Method to determine which O atom site is the hydroxide unit.

An X-ray structure determination of diaspore could readily identify the different Al–O distances in the structure: Al–O1 (2× 1.85 Å; 1× 1.86 Å) and Al–O2 (2× 1.97 Å; 1× 1.98 Å). The relevant bond-valence parameter is $d(1)$ = 1.651 Å for Al(III)–O. Therefore,

$$s_{\text{Al-O1}}(1.85\ \text{Å}) = e^{[(1.651\ \text{Å} - 1.85\ \text{Å})/0.37\ \text{Å}]} = e^{(-0.538)} = 0.584$$
$$s_{\text{Al-O1}}(1.86\ \text{Å}) = e^{[(1.651\ \text{Å} - 1.86\ \text{Å})/0.37\ \text{Å}]} = e^{(-0.565)} = 0.568$$
$$s_{\text{Al-O2}}(1.97\ \text{Å}) = e^{[(1.651\ \text{Å} - 1.97\ \text{Å})/0.37\ \text{Å}]} = e^{(-0.862)} = 0.422$$
$$s_{\text{Al-O2}}(1.98\ \text{Å}) = e^{[(1.651\ \text{Å} - 1.98\ \text{Å})/0.37\ \text{Å}]} = e^{(-0.889)} = 0.411$$

The atomic valences are:

Al(III): 2(0.584) + (0.568) + 2(0.422) + (0.411) = 2.991
O1: 2(0.584) + (0.568) = 1.736
O2: 2(0.422) + (0.411) = 1.255

Both atomic valences for the O atom sites are lower than 2, but the value for O2 is the significantly lower value. Therefore, the O2 sites would be the preferred choice for the location of hydroxide ions in the crystal structure.[41]

(40) *Ionic radii* have been worked out by several researchers, so there are several scales. Two of the most widely used sets of radii originate from Pauling and Shannon.[35, 37] In these two scales, the radius of the oxide ion is set at 1.40 Å (140 pm) and serves as a reference value against which other radii are determined from interatomic distances in various ionic salts. Here is a sampling of Shannon crystal radii (in Å) of several ions for coordination number 6:

Main Group Cations:					**Main Group Anions:**		
Li^+ 0.76	Be^{2+} 0.45				N^{3-} 1.46	O^{2-} 1.40	F^- 1.33
Na^+ 1.02	Mg^{2+} 0.72	Al^{3+} 0.54				S^{2-} 1.84	Cl^- 1.81
K^+ 1.38	Ca^{2+} 1.00	Ga^{3+} 0.62				Se^{2-} 1.98	Br^- 1.96
Rb^+ 1.52	Sr^{2+} 1.18	In^{3+} 0.80	Sn^{4+} 0.69	Sb^{5+} 0.60		Te^{2-} 2.21	I^- 2.20
Cs^+ 1.67	Ba^{2+} 1.35	Tl^{3+} 0.89	Pb^{2+} 0.78	Bi^{5+} 0.76			
	Cu^{2+} 0.73						
Cu^+ 0.77	Zn^{2+} 0.74	Sb^{3+} 0.76					
Tl^+ 1.50	Pb^{2+} 1.19	Bi^{3+} 1.03					

3*d* Cations:						
			Mn^{2+} 0.67 (ls) 0.83 (hs)	Fe^{2+} 0.61 (ls) 0.78 (hs)	Co^{2+} 0.65 (ls) 0.75 (hs)	Ni^{2+} 0.69
Ti^{3+} 0.67		Cr^{3+} 0.62	Mn^{3+} 0.58 (ls) 0.65 (hs)	Fe^{3+} 0.55 (ls) 0.65 (hs)	Co^{3+} 0.55 (ls) 0.61 (hs)	
Ti^{4+} 0.61		Cr^{4+} 0.55	Mn^{4+} 0.53			
			Mn^{5+} 0.33			
		Cr^{6+} 0.44				

[41] R.J. Hill, *Phys. Chem. Miner.* **1979**, *5*, 179-200.

There are some typical rules of thumb for ionic radii:

(a) For isoelectronic ions, radii decrease as the ion charge increases, e.g., O^{2-} (1.40 Å), F^{-} (1.33 Å), Na^{+} (1.02 Å), and Mg^{2+} (0.72 Å);

(b) For a metal ion, radii decrease as its oxidation state increases, e.g., Cr^{3+} (0.62 Å), Cr^{4+} (0.55 Å), and Cr^{6+} (0.44 Å). Also, for a specific oxidation state, the high spin (hs) radius is larger than the low spin (ls) radius;

(c) For any ion, radii increase as its coordination number increases;

(d) For a neutral alkali or alkaline earth atom, its cation radius is smaller by ~0.8 Å, and for a neutral halogen or chalcogen atom, its anion radius is larger by ~0.8 Å;

(e) The radii of anions are generally larger than those of cations, but the values depend on the ion's position in the Periodic Table. For example, the radii of K^{+}, Ba^{2+}, F^{-}, and O^{2-} are all reasonably close to one another. Given their similar sizes, these anions and cations together can form close packings, as seen for oxide perovskites.

One of Pauling's structure-driving rules is that cation-anion radius ratios significantly influence solid-state structures. However, structures do not always follow the optimum radius ratios, as shown by the structure map for MX octet compounds in Slide #**32**. For example, consider the NaCl-type structures for MgO (a = 4.20 Å; R_+/R_- = 0.46), BaO (a = 5.53 Å; R_+/R_- = 0.96), BaTe (a = 6.9 Å; R_+/R_- = 0.61), and a hypothetical "MgTe" (R_+/R_- = 0.29). The ideal radius ratio R_+/R_- is 0.414 for octahedral coordination and only R_+/R_- for MgO is close to this value. As a result, if the ions are modeled as hard spheres, the oxide anions in MgO are nearly close packed and the magnesium cations fit snugly in the octahedral voids. In BaTe, the Ba^{2+} ions are somewhat large for the octahedral voids, so the telluride anions become separated and are not strictly close packed. This effect gets further exaggerated in BaO because the ions have nearly equal ionic radii. On the other hand, for the hypothetical NaCl-type "MgTe", the Mg^{2+} ions are too small for the octahedral voids of telluride ions, and would "rattle around" inside these holes. Cation rattling is an important phenomenon to suppress thermal conductivity in solids and is a feature of some thermoelectric materials.[42] In fact, MgTe is reported to adopt the wurtzite (ZnO)-type structure with tetrahedrally coordinated Mg^{2+} ions rather than the NaCl-type structure and forms the hexagonal NiAs-type structure under pressure. Theory also predicts this structure type to be more stable than the NaCl-type.[43]

If the structures of ionic compounds were based solely on sphere packings of anions, we might expect that unit cell sizes for a given anion would be nearly independent of the cation component, but that is definitely not observed. Nonetheless, ionic structures do have characteristics of 3-d close packings of spheres. In fact, given that anion–anion electrostatic interactions are inherently repulsive and isotropic, the lowest energy structure for an ionic solid arises by maximizing the unit cell volume for fixed values of cation–anion distances, an outcome that will minimize the anion–anion repulsions.[44] As a result, the term *eutaxy* (from the Greek *ενтακτοζ*, which translates as "well ordered") has been proposed to convey arrangements consistent with close packings in ionic and polar-covalent extended structures.

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[42] D.J. Voneshen, K. Refson, E. Borissenko, M. Krisch, A. Bosak, A. Piovano, E. Cemal, M. Enderle, M.J. Gutmann, M. Hoesch, M. Roger, L. Gannon, A.T. Boothroyd, S. Uthayakumar, D.G. Porter, J.P. Goff, *Nature Mater.* **2013**, *12*, 1028-1032.

[43] T. Li, H. Luo, R.G. Greene, A.L. Ruoff, S.S. Trail, F.J. DiSalvo, *Phys. Rev. Lett.* **1995**, *74*, 5232-5235.

[44] M. O'Keeffe, *Acta Cryst. Sect. A* **1977**, *A33*, 924-927.