Ionic Radii for Group 1 and Group 2 halide, hydride, fluoride, oxide, sulphide, selenide and telluride crystals

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Summary

This paper discusses the calculation of internuclear distances by a soft-sphere ionic radii model for twenty crystalline Group 1 halides and hydrides and three ammonium halides with either sodium chloride or caesium chloride structures. It also describes calculation of internuclear distances with the soft-sphere model for three crystalline Group 2 fluorides with fluorite structures and fifteen Group 2 crystalline binary salts (oxides, sulphides, selenides and tellurides) with sodium chloride structures. Soft-sphere calculated radii for Group 1 salts are compared with other theoretical radii. Soft-sphere calculated results agree very well with experimental measurements in all cases except for lithium hydride. The probable reason for the discrepancy with lithium hydride and merits of the soft sphere model are discussed. A simple expression to calculate lattice energies using the soft-sphere radii concept is given and results compared well with lattice energies calculated by the Born-Haber cycle.

Introduction

When atoms or ions approach each other in the solid state they take up equilibrium positions where the forces of attraction, such as chemical bonding, just balance the forces of repulsion. The sizes of the atoms or ions must then be finite and there is some significance in terms of ionic radius. The concept of ionic radius is useful for understanding the differences in lattice energies and interpreting variations in crystal structures of ionic compounds. Values of ionic radii are mainly calculated from semi-empirical methods or obtained from measurements made on ionic crystals. The most familiar approach to ionic radii is the hard-sphere model. Many authors have produced tables of hard-sphere ionic radii[1,2]. These radii are constant for a particular charge and in some cases the co-ordination number. Some radii regularly referred to were developed by Pauling and a common standard source for (hard sphere) ionic radii is produced by Shannon[3].

Hard sphere model

The most familiar approach to ionic radii is the hard-sphere model where the cation and anion can be represented as hard spheres and assumed to be in contact. A common method is to assume that the radius ratio of the positive ion to that of the negative ion is a function of the reciprocal of the "effective nuclear charge" of the two respective ions[4]. Although the traditional sets of hard sphere radii provided estimates of the size of atomic ions they are unable to reproduce observed inter-atomic distances produced by modern structural analysis[5]. What is more significant is that with the hard sphere model, the size of an ion is constant for a particular charge and co-ordination number. For example, the radius of Na^+ ion is considered to be constant in NaF, NaCl, NaBr or NaI even though the proton number and size of the anions are different. The hard sphere model implies that the attractive forces between a particular cation and an anion (no matter what size or which period they are in) with an identical opposite charge is constant.

Soft sphere approach

An alternative model proposed originally in 1978 was developed in 2004[6]. The cation and anion are considered to be overlapping or deformable soft spheres. Internuclear separations are calculated from the relationship:

$$s(calc)^k = [M]^k + [X]^k$$

where s is the internuclear separation, [M] and [X] are radii of cations and anions respectively, and k is a constant for the particular type of ionic compound and is an indication of the amount of overlap or ion deformability, the bigger the value of k the larger the overlap between the cation and anion.

This method produced ionic radii that agreed well with experimental separations for Group 1 metal halides (excluding ammonium halides) with sodium chloride structures[6]. However, the sets of radii developed were unable to generate calculated results that give good agreement with experimental measurements of Group 1 metal hydrides nor with halides with caesium chloride structures. This paper proposes new radii that give good agreement and extends the model to include Group 1 hydrides with sodium chloride structures, Group 1 halides with caesium chloride structures, as well as Group 2 oxides, sulphides, selenides and tellurides with sodium chloride structures and calcium, strontium and barium fluoride which possess fluorite structures. The new radii introduced in this work also produce good agreement for ammonium chloride and bromide which have caesium chloride structures and ammonium iodide which has sodium chloride structure at room temperature.

Comparison between calculated and observed internuclear separations

Since it was shown that calculations using early historical ionic radii provided poor agreement with observed values[6], a later set of hard sphere radii[7,8] is chosen in this work to produce internuclear distances for Group 1 halides.   Table 1 lists the hard sphere radii and soft sphere radii for Group 1 used in this work. In this work, all experimental and calculated results are given in angstrom units, where 1 Å = 10^{-10} m. The root mean square (r.m.s.) deviation δ is given at the top of each appropriate table.

Table 1. Ionic radii (Å) for NH_4^+ and Group 1 metal halide and hydride crystals

| Waddington (hard sphere) | | | | Soft Sphere | | | |
Cation	Radius	Anion	Radius	Cation	Radius	Anion	Radius
Li^+	0.793			Li^+	1.094	H^-	1.399
Na^+	1.009	F^-	1.322	Na^+	1.497	F^-	1.547
K^+	1.320	Cl^-	1.822	K^+	1.971	Cl^-	2.181
Rb^+	1.460	Br^-	1.983	Rb^+	2.160	Br^-	2.372
Cs^+	1.718	I^-	2.241	Cs^+	2.368	I^-	2.668
				NH_4^+			2.107

In Table 2, observed internuclear separations[9] are shown in column (A), separations calculated using the traditional hard sphere model are given in column (B) and differences between experimental and calculated separations are given in column (C).   The calculated results using the hard sphere radii differ from observed by bigger than 0.01 Å in thirteen out of the twenty Group 1 halides.

Internuclear separations calculated from soft sphere radii have the exponent *k* being equal to 5/3 (or 1.66667) for Group 1 halides with sodium chloride structures, *k* equal to 4/3 (1.33333) for Group 1 hydrides and k equal to 17/11 (1.545455) for halides with caesium chloride structures. The internuclear distances calculated from the soft sphere model compared with observed values for Group 1 metal halides and ammonium iodide which possesses the same crystal structure are provided in Table 3.   The results calculated from soft sphere radii differ from observed values by less than 0.01 Å in all of the eighteen halides with just over half of them differing by 0.005 Å or less.

Table 2. Observed and hard sphere radii calculated internuclear separations for Group 1 halides

Crystal	Internuclear separation (Å) rounded to 3 decimal places		δ = 0.0247 Å
	Observed	Calculated(hard sphere)	Obs. –Calc.
	(A)	(B)	(C)
LiF	2.013	2.061	-0.048
LiCl	2.570	2.561	0.009
LiBr	2.751	2.722	0.029
LiI	3.006	2.980	0.026
NaF	2.314	2.331	-0.017
NaCl	2.820	2.831	-0.011
NaBr	2.987	2.992	-0.005
NaI	3.238	3.250	0.012
KF	2.672	2.642	0.030
KCl	3.146	3.142	0.004
KBr	3.300	3.303	-0.003
KI	3.533	3.561	-0.028
RbF	2.827	2.782	0.045
RbCl	3.295	3.282	0.013
RbBr	3.434	3.433	-0.009
RbI	3.670	3.701	-0.031
CsF	3.001	3.040	-0.039
CsCl	3.569	3.540	0.029
CsBr	3.720	3.701	0.019
CsI	3.955	3.959	-0.004

Table 3. Observed and soft sphere calculated internuclear separations for halides with NaCl structures

Crystal	Internuclear separation (Å) rounded to 3 decimal places		δ = 0.00559 Å
	Observed	Calculated(soft sphere)	Obs. –Calc.
	(A)	(B)	(C)
LiF	2.013	2.021	-0.008
LiCl	2.570	2.572	-0.002
LiBr	2.751	2.744	0.007
LiI	3.006	3.015	-0.009
NaF	2.314	2.307	0.007
NaCl	2.820	2.819	0.001
NaBr	2.987	2.982	0.005
NaI	3.238	3.239	-0.001
KF	2.672	2.679	-0.007
KCl	3.146	3.149	-0.003
KBr	3.300	3.300	0.000
KI	3.533	3.542	-0.009
RbF	2.827	2.835	-0.008
RbCl	3.295	3.290	0.005
RbBr	3.434	3.437	-0.003
RbI	3.670	3.672	-0.002
CsF	3.001	3.010	-0.009
NH_4I	3.630	3.635	-0.005

Table 4 shows internuclear distances calculated from the soft sphere ionic model together with observed values for Group 1 hydrides. Comparisons of Group 1 halides with caesium chloride structures

(including two ammonium halides) are shown in Table 5. All the results showed agreement to better than 0.01 Å with the exception of lithium hydride.

Table 4. Internuclear separations for Group 1 hydrides

Crystal	Internuclear separation (Å) rounded to 3 decimal places			$\delta = 0.00763$ Å (LiH excluded)
	Observed	Calculated(soft sphere)	Obs. –Calc.	
	(A)	(B)	(C)	
LiH	2.043	2.102	-0.059	
NaH	2.441	2.436	0.003	
KH	2.855	2.847	0.008	
RbH	3.025	3.016	0.009	
CsH	3.195	3.203	-0.008	

Choice of ionic radii

We first derived Na^+, Rb^+ and Cl^- radii based on electron density measurements[10,11] and then generated the other radii which in combination with the first 3 produced good results. The particular set of soft sphere ionic radii, as given in Table 1, reproduced internuclear separations that matched observed values of both halides and hydrides. The ions maintain the following order of size:

$Li^+ < H^- < Na^+ < F^- < K^+ < Cl^- < Rb^+ < Br^- < Cs^+ < I^-$
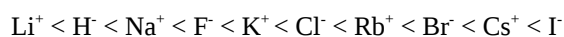
All the anions are larger than isoelectronic cations, but the Pauling order of ion size is not followed. There is no reason to assume that K^+ is smaller than F^- especially that fluorine is the most electronegative element. It is reasonable to suppose that the size of fluorine would increase slightly after gaining an electron to become F^-. The N-H bond length in NH_4X has been determined[12] to be about 1.03 Å, the Bohr radius is about 0.53 Å, so as a first approximation, the ionic radius of NH_4^+ was estimated to be $1.03 + 2 \times 0.53 = 2.09$ Å.(2×0.53 is added to include the size of nitrogen and hydrogen). To produce better agreement, this figure was modified to 2.107 Å which was used in the calculations.

Table 5. Internuclear separations for halides with CsCl structures

Crystal   Internuclear separation (Á) rounded to 3 decimal places   δ = 0.00646 Á

Crystal	Observed (A)	Calculated(soft sphere) (B)	Obs. –Calc. (C
CsCl	3.569	3.563	0.006
CsBr	3.720	3.711	0.009
CsI	3.955	3.947	0.008
NH_4Cl	3.357	3.358	-0.001
NH_4Br	3.515	3.510	0.005

Data from electron density maps

Electron density shows how electrons are distributed, it is a continuous function that is experimentally observable and provides a better physical picture of the nature of the chemical bonding than other models. Electron density maps are experimentally determined from X ray diffraction where electron density minima provide a very good indication of ionic size (or internuclear separation)[13]. As shown in Table 6, the ratios of the size of ions derived from electron density maps for Li^+ to F^- [14], Na^+ to Cl^-[10], K^+ to Cl^-[8], Rb^+ to Cl^-[11] and K^+ to Br^-[15] correspond much closer with soft sphere radii than those of the respective hard sphere radii.

Table 6. Comparison of cation/anion (r^+/r-) radius ratio.

|	Pauling			Waddington			Electron Density			This Work		
	Cation	Anion	r^+/r^-	Cation	Anion	r^+/r^-	Cation	Anion	r^+/r^-	Cation	Anion	r^+/r^-
LiF	0.60	0.95	0.44	0.739	1.322	0.56	0.92	1.09	0.84	1.094	1.547	0.71
NaCl	0.95	1.81	0.52	1.009	1.822	0.55	1.17	1.64	0.71	1.497	2.181	0.69
KCl	1.33	1.81	0.73	1.320	1.822	0.72	1.45	1.70	0.85	1.971	2.181	0.90
RbCl	1.48	1.81	0.82	1.460	1.822	0.80	1.71	1.58	1.08	2.160	2.181	0.99

| KBr | 1.33 | 1.95 | 0.68 | | 1.320 | 1.983 | 0.67 | 1.57 | 1.73 | 0.91 | | 1.971 | 2.372 | 0.83 |

Soft sphere model for Group 2

Calcium, strontium and barium fluoride possess fluorite structures and the exponent k equals 9/5 or 1.8 is used in the calculations. The oxides, sulphides, selenides of magnesium, calcium, strontium and barium together with tellurides of calcium, strontium and barium have sodium chloride structures. A different exponent k which is equal to 8/5 or 1.6 is used to calculate the internuclear distances for these binary compounds. Beryllium oxide has a hexagonal prismatic structure, beryllium sulphide, selenide and telluride possess other structures and are excluded from the following calculations.

Choice of radii

The ionic radius of F^- for the soft sphere model is kept the same as the value which is used in calculating Group 1 halides although the coordination number is different for the fluoride ion in the Group 2 fluorides with fluorite structure. We produced an Mg^{2+} radius based on electron density measurements[16] which showed that magnesium in magnesium sulphide has an effective electron distribution radius of 1.28 Å. This figure was modified to 1.282 Å which produces better results. We then generated the other radii which in combination with the Mg^{2+} radius produced internuclear distances which matched closely with the observed. The particular set of soft sphere ionic radii is given in Table 7. The ions maintain the following order of size:

$$Mg2^+ < O^{2-} < F^- < Ca^{2+} < Sr^{2+} < S^{2-} < Ba^{2+} < Se^{2-} < Te^{2-}$$
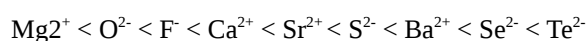
As with Group 1, all the anions are larger than isoelectronic cations.

Table 7. Soft sphere Ionic radii (Å) for Group 2 fluoride, oxide, sulphide, selenide and telluride crystals

				Soft Sphere				
Cation	Radius		Anion	Radius	Cation	Radius	Anion	Radius
Mg^{2+}	1.282		F^-	1.547	Ca^{2+}	1.657	O^{2-}	1.452
Sr^{2+}	1.861		S^{2-}	2.053	Ba^{2+}	2.084	Se^{2-}	2.179
							Te^{2-}	2.440

Table 8 lists the experimental internuclear separations and soft sphere radii calculated separations for Group 2 fluorides, oxides, sulphides and tellurides with sodium chloride structures. There is very good agreement between the two sets of values. Internuclear separations calculated from soft sphere radii differ from

experimental values by less than 0.01 Å in all except one of the fifteen compounds. Agreement is less good only for calcium selenide which shows a difference of 0.012 Å with the observed. Agreement for seven out of the fifteen was to 0.005 Å or better.

Table 8. Observed and soft sphere calculated internuclear separations for Group 2 MO, MS, MSe, MTe

Crystal	Internuclear separation (Å) rounded to 3 decimal places		δ = 0.00660 Å
	Observed	Calculated(hard sphere)	Obs. –Calc.
	(A)	(B)	(C)
MgO	2.107	2.111	-0.004
MgS	2.602	2.597	0.004
MgSe	2.731	2.722	0.009
CaO	2.406	2.400	0.006
CaS	2.851	2.856	-0.005
CaSe	2.962	2.974	-0.012
CaTe	3.186	3.194	-0.008
SrO	2.572	2.566	0.006
SrS	3.012	3.006	0.005
SrSe	3.123	3.121	0.002
SrTe	3.333	3.335	-0.002
BaO	2.762	2.753	0.009
BaS	3.184	3.176	0.008
BaSe	3.295	3.288	0.007
BaTe	3.500	3.495	0.005

The experimental internuclear distances for calcium, strontium and barium fluorides and values calculated from soft sphere radii are shown in Table 9. A comparison of the results show that all three of the calculated results agree with the observed to better than 0.01Å.

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Table 9. Observed and soft sphere calculated internuclear separations for Group 2 fluorides.

Crystal   Internuclear separation (Å) rounded to 3 decimal places $\delta = 0.00783$ Å

	Observed (A)	Calculated(soft sphere) (B)	Obs. –Calc. (C)
CaF_2	2.365	2.356	-0.009
SrF_2	2.509	2.513	-0.004
BaF_2	2.683	2.692	-0.009

Lattice energies

The lattice energy of a compound at 0^oK may be defined as the energy change when one mole of the compound at one atmosphere pressure is converted into gaseous ions which are separated from each other at infinity. Lattice energies can be calculated normally using the Born-Haber cycle or from equations such as the Born-Lande and Born-Mayer equations or the improved Kapustinskii[17] equation.

In the soft sphere ionic model, the two or more ions of a compound in a crystal lattice are deformed and overlap each other. Therefore, the lattice energy is the energy required to overcome this overlap or interpenetration of the ions, which can be approximated as the energy required to remove the electron(s) bonding the ions in the overlap space. The lattice energy can then be calculated if the relative sizes and relative overlap of the ions are known, plus if the energy to remove an electron (dissociate) from a standard species is known. With the soft sphere model, the degree of overlap is a function of k, where k is the appropriate constant for each type of compound. For example, k is 1.66667 (or 5/3) for alkali metal halides with sodium chloride structures and k is 1.3333 (or 4/3) for alkali metal hydrides. The most simple species is hydrogen with only one electron and the Rydberg constant is accurately calculated.

Based on these simple assumptions we have developed a very simple equation to calculate the lattice energy of ionic compounds.   The expressiom is:

$$\textit{(Lattice energy) } E_L = R(H_o/M)(M^{k-1})/(X^{k-1.3333})(\tfrac{1}{2}^{\,0.33333})(\Sigma Q_i^2)$$

R is the Rydberg constant for infinite mass converted to kilo Joules per mole, H_o is the classical Bohr radius, M is the size of the cation, X is the size of the anion and Q_i is the charge on the ions. Hence, for sodium chloride $\Sigma Q_i^2 = 1 + 1 = 2$ and for calcium fluoride it is $4 + 1 + 1 = 6$ etc. R is the amount of energy needed to remove an electron from a species the size of a hydrogen atom, (H_o/M) provides a ratio of the distance of the electron from the nucleus, since the greater the size the less is the energy needed to remove the electron. $(M^{k-1})/(X^{k-1.3333})$ gives an approximation of the overlap, this is multiplied by a factor which is approximated to ($\tfrac{1}{2}^{\,0.33333}$) because the electron is not removed to infinity away from both ions (but rather removed from the overlap region). ΣQ_i^2 is the sum of all the squares of the charges on the ions, since the higher the charge on the ions the more electrons need to be removed from the overlap region and the more energy is required to separate them. The lattice energies of ionic Group 1 and Group 2 compounds, where the soft sphere radii are known, are calculated from this equation and the results are listed in Table 10. and compared with lattice calculated from the Born-Haber cycle and published in the CRC Handbook of Chemistry and Physics[18]. Column (A) of Table 10 gives the formula of the ionic crystal, column (B) shows the results calculated from the Born-Haber cycle, column (C) shows the lattice energies calculated from the soft sphere equation and column (D) of the table shows the absolute difference between the Born-Haber value and the value from our equation expressed as a percentage. The lattice energies are given in kilo Joules per mole and we have shown only those values of lattice energies where there is a counterpart available in the CRC Handbook of Chemistry and Physics (2008-2009). For example, results of all the alkali metal halides are shown but lattice energies for CaS, SrS, and BaS are not calculated and excluded from the table because these are not available in the CRC Handbook. Lithium hydride is also excluded because it has appreciable covalent character.

Table 10. Lattice energies calculated from the Born-Haber cycle and by the soft sphere equation

Crystal	Born-Haber	Soft-sphere	Abs % difference
(A)	(B)	(C)	(D)
LiF	1030	924.9	10.2

LiCl	834	824.8	1.1
LiBr	788	802.1	1.8
LiI	730	771.3	5.7
NaF	910	833.1	8.5
NaCl	769	743.0	3.4
NaBr	732	722.5	1.3
NaI	682	694.7	1.9
KF	808	760.1	5.9
KCl	701	677.9	3.3
KBr	671	659.2	1.8
KI	632	633.8	0.3
RbF	774	737.3	4.7
RbCl	680	657.5	3.3
RbBr	651	639.4	1.8
RbI	617	614.8	0.4
CsF	744	715.0	3.9
CsCl	657	631.3	3.9
CsBr	632	620.2	1.9
CsI	600	604.9	0.8
NaH	807	842.3	4.4
KH	711	701.2	1.4
RbH	686	659.6	3.8
CsH	648	620.4	4.3
CaF_2	2640	2438.3	7.6
SrF_2	2476	2382.4	3.4
BaF_2	2347	2329.0	0.8
MgO	3795	3613.9	4.8
MgSe	3071	3243.2	5.6
CaO	3414	3261.4	4.5
CaSe	1745	2926.8	2.4

CaTe	2721	2839.8	4.4
SrO	3217	3113.4	3.2
SrSe	2736	2794.0	2.1
BaO	3029	2975.5	1.8
BaSe	2611	2670.2	2.3

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The Exponent *k*

We consider the exponent *k* is governed by the degree of "overlap" or "deformation" of the ions and made five empirical and general assumptions: (a) *k* is greater than 1; (b) it is a simple fraction, e.g. 7/4 or 5/3; (c) for ions with a one to one ratio (e.g. NaCl or MgO) the overlap is biggest between the most positive and most negative ions, i.e. alkali metal halides but much smaller for hydrides since the hydride ion is much less negative than halides; (d) overlap is bigger when a doubly charged positive ion bonds with most negative anions; (e) overlap is greater when the coordination number is lower. We began by applying 4/3 to the equations and then 5/3 and so on until we were able to obtain good agreement for the group 1 and group 2 compounds listed above.

Discussion

Lithium hydride appears to be anomalous. The lithium ion being very small is likely to have a tendency to distort the electron cloud of the hydride ion and leads to a covalent character of the bond. It has been reported that the compound has appreciable covalent character[19]. The electron density map of lithium hydride also shows there is covalent bonding joining lithium and hydrogen[20]. Since the bonds between the different heteronuclear diatomic halides may not be perfectly ionic it is not surprising that there is no perfect agreement between observed internuclear separations and those calculated from the soft sphere model.

Cordero[21] et al recently produced a comprehensive list of covalent radii. We have made a comparison between the set of covalent radii with our group 1 soft sphere radii. As listed in Table 10, although there are some similarities they are different enough to show that they serve different purposes. As expected, the covalent radii for all five metals are bigger than the corresponding ionic radii since all the metal ions have one electron less. Similarly, the ionic radii for the halides are larger than the corresponding covalent radii. However, it is a bit surprising that the differences between the covalent and ionic radii for the halogens are much greater than that of the metals. It is probable that this is due to the first ionisation energies of the alkali metals being bigger than the first electron affinities of the halogens (i.e. the outermost electron of the alkali metals is more tightly bound to

the atom and the size of the ion after ionisation is only slightly smaller, whereas the electron affinities of the

halogens are smaller which means that the extra electron is only loosely bound and the size of the anion

becomes much greater) although this is only a hypothesis and has no theoretical proof.

Table 10. Comparison of univalent covalent radii and soft sphere ionic radii (Å)

Metal	Covalent Radius	Soft Sphere Ionic Radius	Halogen	Covalent Radius	Soft Sphere Ionic Radius
Li	1.28	1.094	F	0.57	1.547
Na	1.66	1.497	Cl	1.02	2.181
K	2.03	1.971	Br	1.20	2.372
Rb	2.20	2.160	I	1.39	2.668
Cs	2.44	2.368			

Soft sphere ionic radii are not consistent with the traditional radius ratio rules[22]. The radius ratio rules are not

reliable and must be used with great care and "more in the spirit of a first guess than a predictive tool"[23]. They

predict the wrong structures for many Group 1 metal halides and had been described as "particularly

unhelpful"[24]. Hence, when the soft sphere model was developed the rules were not taken into consideration.

The lattice energies calculated from the soft sphere equation provide good agreement with those calculated by

the Born-Haber cycle. Of the 36 compounds listed in Table 7, only 1 differ by 10.2 % and 30 of them (or 83.3%

of the total) agree to within 5% or better and the remaining 5 differ between 5% and 10%. Although agreement

between the soft sphere equation or other type of equation with Born-Haber cycle lattice energies does not

constitute proof the validity of a soft sphere or hard sphere model[25].

Conclusion

In contrast to traditional hard sphere radii, we have shown that internuclear separations calculated from soft

sphere radii produce excellent agreement with experimental values for ammonium halides, all Group 1 halides

and hydrides with sodium chloride and caesium chloride structures except lithium hydride which exhibit

covalent character. A comparison of cation to anion ratios between values obtained from electron density

measurements and calculated values also show that soft sphere ionic radii provide better agreement.

Internuclear distances for Group 2 fluorides with fluorite structures and Group 2 oxides, sulphides, selenides

and tellurides with sodium chloride structures are also accurately calculated by soft sphere radii. In addition,

lattice energies calculated by the soft sphere equation also agree well with Born-Haber cycle energies. This

work provides strong evidence that the concept of soft deformable and overlapping spheres in ionic crystals is a much better physical representation than the hard sphere model and there is good indication that ionic radii, even in compounds where the coordination number is constant such as in alkali metal halides, are not additive. When ions approach each other in the solid state they overlap each other when they reach the equilibrium positions and the shapes of the ions are deformed and not spherical.   Ions do not behave as hard spheres but as deformable shapes (that resemble may be an egg or a chestnut). The degree of overlap, or deformation of the ion from a spherical shape, depends on the kind of structure, the co-ordination number and type of compound.

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