Soft-sphere Ionic Radii for Group 1 and Group 2 Metal Halides and Ammonium Halides

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Soft-sphere ionic radii, *M* and *X*, are used to derive internuclear distances, *d*, in cubic crystalline Group 1 and Group 2 metal halides and crystalline ammonium halides from the relation $d^{\frac{5}{3}} = M^{\frac{5}{3}} + X^{\frac{5}{3}}$. Soft-sphere radii for metal ions are identical to metallic radii for twelve-co-ordination.

SIMPLE models treat metals as three-dimensional arrays of cationic islands in electronic seas, but the implied relation between metallic radii in elements and ionic radii in salts has not been explored.

RESULTS AND DISCUSSION

Metallic Radii.—Metals in Groups 1 and 2 of the Periodic Table form body-centred cubic (b.c.c.) and/or face-centred cubic, *i.e.*, cubic close-packed (c.c.p.) and/or hexagonal close-packed (h.c.p.) crystals.[1,2] Table 1 contains unit-cell dimensions, a_0 (with c_0 for h.c.p. as footnotes), selected from ref. 3 and metallic radii for eight co-ordination, $R[8] = a_0 3^{\frac{1}{2}}/4$ (b.c.c.), and twelve-co-ordination, $R[12] = a_0 2^{\frac{1}{2}}/4$ (c.c.p.) or $\{a_0 + [(a_0^2/3) + (c_0^2/4)]^{\frac{1}{2}}\}/4$ (h.c.p.), derived on the assumption that approximately spherical ions are in contact.

Metallic radii for twelve-co-ordination are similar for h.c.p. and c.c.p. structures, where transitions occur without significant volume changes. Transitions from close-packed to b.c.c. structures involve increases in volume of *ca.* 3.2%. Hence, the metallic radii are related by $R[12] = (4 \times 6^{\frac{1}{2}}/9 \times 1.032)^{\frac{1}{3}}R[8] = 1.018R[8]$. The factor $(4 \times 6^{\frac{1}{2}}/9)^{\frac{1}{3}} \approx 1.03$ would apply to transitions at constant volume.[2] Our values of $R[12]$ for Group 1 and Group 2 metals are reasonably close to those of Pauling[1] and Wells[2] (Table 1), even when derived from different experimental data.

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[1] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University, Ithaca, New York, 1960, p. 403.

[2] A. F. Wells, 'Structural Inorganic Chemistry,' 4th edn., Clarendon, Oxford, 1975, pp. 1020—1022.

[3] J. D. H. Donnay and H. M. Ondik, eds., 'Crystal data,' vol. 2, 3rd edn., U.S. Department of Commerce, National Bureau of Standards, and Joint Committee on Powder Diffraction Standards, Washington, D.C., 1973.

TABLE 1

Metallic radii (Å)

	Body-centred cubic		Close packed			Pauling	Wells	Soft sphere
Metal	a_0	$R[8]$		a_0	$R[12]$	$R[12]$	$R[12]$	$M[6]$
Li	3.509 4	1.520	c.c.p.	4.379	1.548	1.549	1.57	1.548
Na	4.290 6	1.858	c.c.p.	5.350	1.892	1.896	1.91	1.889
			h.c.p.	3.767 [a]	1.884			
K	5.21	2.256			2.297 [b]	2.349	2.35	2.298
Rb	5.63	2.438			2.482 [b]	2.48	2.50	2.480
Cs	6.067	2.627			2.674 [b]	2.67	2.72	2.676
								$M[8]$
Be	2.551 5	1.105	h.c.p.	2.281 3 [c]	1.126	1.123	1.12	
Mg		1.570 [b]	h.c.p.	3.202 2 [d]	1.598	1.598	1.60	
Ca	4.477	1.939	c.c.p.	5.575	1.971	1.970	1.97	1.974
			h.c.p.	3.94 [e]	1.971			
Sr	4.85	2.100	c.c.p.	6.04	2.135	2.148	2.15	2.139
Ba	5.025	2.176			2.215 [b]	2.215	2.24	2.327

[a] $c_0 = 6.154$ Å. [b] Estimated from $R[12] = 1.018R[8]$. [c] $c_0 = 3.5773$ Å. [d] $c_0 = 5.1991$ Å. [e] $c_0 = 6.44$ Å.

TABLE 2

Ionic radii (Å)

	Hard sphere [4-6]		Soft sphere		
Ion	Goldschmidt	Pauling	$M[4]$	$M[6]$	$M[8]$
Li^+	0.78 *	0.60		1.548	
Na^+	0.98	0.95		1.889	
K^+	1.33	1.33		2.298	
Rb^+	1.49	1.48		2.480	
Cs^+	1.65	1.69		2.676	2.764
$[NH_4]^+$	1.43	1.48	2.356	2.426	2.506
Ca^{2+}	1.06	0.99			1.974
Sr^{2+}	1.27	1.13			2.139
Ba^{2+}	1.43	1.35			2.327
			$X[4]$	$X[6]$	$X[8]$
F^-	1.33	1.36	1.054	1.085	
Cl^-	1.81	1.81	1.839	1.835	1.896
Br^-	1.96	1.95		2.053	2.121
I^-	2.20	2.16		2.363	2.441

* Ref. 4 gives 0.70 Å.

TABLE 3

Internuclear distances (Å) for sodium chloride structures

		d			This work	
Salt	a_0	(obs.)	Goldschmidt	Pauling	d(calc.)	d(obs.) $-d$(calc.)
LiF	4.026 2	2.013	2.11	1.96	2.016	−0.003
LiCl	5.139 88	2.570	2.59	2.41	2.570	0.000
LiBr	5.501	2.750	2.74	2.55	2.747	0.003
LiI	6.012	3.006	2.98	2.76	3.007	−0.001
NaF	4.623	2.311	2.31	2.31	2.308	0.003
NaCl	5.640 2	2.820	2.79	2.76	2.822	−0.002
NaBr	5.974	2.987	2.94	2.90	2.989	−0.002
NaI	6.475	3.237	3.18	3.11	3.236	0.001
KF	5.344	2.672	2.66	2.69	2.673	−0.001
KCl	6.292 94	3.146	3.14	3.14	3.145	0.001
KBr	6.599	3.300	3.29	3.28	3.301	−0.001
KI	7.065 55	3.533	3.53	3.49	3.533	0.000
RbF	5.64	2.820	2.82	2.84	2.838	−0.018
RbCl	6.590	3.295	3.30	3.29	3.294	0.001
RbBr	6.890 8	3.445	3.45	3.43	3.446	−0.001
RbI	7.340	3.670	3.69	3.64	3.671	−0.001
CsF	6.04	3.020	2.98	3.05	3.018	0.002
$[NH_4]I$	7.259	3.630	3.63	3.64	3.630	0.000

Hard-sphere Ionic Radii.—The well known Goldschmidt [4,5] and Pauling [5,6] ionic radii for cations of Groups 1 and 2 and anions of Group 7 are listed in Table 2. It is generally supposed that ions in crystalline salts behave as fairly hard spheres with nearly constant radii. If this were so, internuclear distances would be reproduced with reasonable accuracy by the sum of cationic and anionic radii.

Sodium chloride structures. Unit-cube dimensions selected from ref. 3 for Group 1 halides having NaCl structures and the corresponding internuclear distances,

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[4] V. M. Goldschmidt, 'Geochemistry,' Clarendon, Oxford, 1954, pp. 88—89.

[5] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, London, 1972, p. 52.

[6] Ref. 1, pp. 514, 518.

$d = a_0/2$, are compared in Table 3 with internuclear distances calculated from Goldschmidt and Pauling ionic radii. Agreement between observed and calculated internuclear distances is poor. The differences are rarely less than 0.01 Å and are sometimes more than 0.05 Å.

Furthermore, differences between observed internuclear distances for pairs of metal halides with a common ion, [d(M ··· X) − d(M ··· X′)] and [d(M ··· X) − d(M′ ··· X)], vary systematically with the size of the common ion (except where rubidium fluoride is involved). The differences in Table 4 illustrate that it is impossible for any set of hard-sphere radii to reproduce observed internuclear distances within the limits of experimental accuracy, say <0.005 Å. It is clear that the hard-sphere model is unsatisfactory unless elaborate correction factors are applied.[7]

TABLE 4

Differences between observed internuclear distances (Å) for pairs of salts with a common ion

Common ion	$Cl^- - F^-$	$Br^- - Cl^-$	$I^- - Br^-$
Li^+	0.557	0.180	0.256
Na^+	0.509	0.167	0.250
K^+	0.474	0.154	0.233
Rb^+	0.475	0.150	0.225
	$Na^+ - Li^+$	$K^+ - Na^+$	$Rb^+ - K^+$
F^-	0.298	0.361	0.148
Cl^-	0.250	0.326	0.149
Br^-	0.237	0.313	0.145
I^-	0.231	0.296	0.137

Soft-sphere Ionic Radii.—An alternative soft-sphere model for ionic crystals is considered here. The ions resemble soft spherical balloons with charges at the centres, so that compression occurs when ions of opposite charge are in contact.

It is proposed that internuclear distances, d, are related to soft-sphere radii, M (cations) and X (anions), by $d^k = M^k + X^k$, where k is a constant characteristic of the class of compound. The special case of $k = 1$ would correspond to the hard-sphere model; the special case of $k = 2$ would correspond to a 90° angle of compression. We shall examine the special case of $k = \frac{5}{3}$ because differences between values of $d^{\frac{5}{3}}$ for pairs of halides having similar structures and a common ion are reasonably constant and without systematic variations.

Sodium chloride structures. Values of $d^{\frac{5}{3}}$ for Group 1 halides with NaCl structures are separated into cationic and anionic components by assuming that soft-sphere radii for metal ions are proportional to metallic radii. Plots of $d^{\frac{5}{3}}$ against $R[12]^{\frac{5}{3}}$ give four parallel straight lines with gradients of 1.00, suggesting that soft-sphere cationic radii are equal to metallic radii. The intercepts of 1.146, 2.750, 3.316, and 4.192 correspond to values of $X^{\frac{5}{3}}$.

The resulting soft-sphere ionic radii for six-co-ordination, $M[6]$ and $X[6]$, are listed in Table 2. They are used to derive internuclear distances from the relation $d^{\frac{5}{3}} = M[6]^{\frac{5}{3}} + X[6]^{\frac{5}{3}}$. The differences between observed and calculated internuclear distances in Table **3** are ⩽0.003 Å, except in the case of RbF.

Rubidium fluoride. The original report of the cell dimensions of rubidium fluoride[8] gives a_0 5.64 Å. We are unable to trace any recent measurements. Our calculated length of the unit cube is a_0 5.676 Å.

Caesium chloride structures. Soft-sphere radii in Table 2 for caesium and halide ions with six- and eight-co-ordination are related by $M[8] = 1.033M[6]$ and $X[8] = 1.033X[6]$. The factor 1.04 is used elsewhere.[9]

Unit-cube dimensions[3] for halides with CsCl structures and the corresponding internuclear distances, $d = a_0 3^{\frac{1}{2}}/2$, are compared in Table 5 with internuclear distances calculated from the relation $d^{\frac{5}{3}} = M[8]^{\frac{5}{3}} + X[8]^{\frac{5}{3}}$. Differences between observed and calculated internuclear distances are ⩽0.003 Å.

TABLE 5

Internuclear distances (Å) for CsCl, $[NH_4]F$, and CaF_2 structures

Salt	a_0	d(obs.)	d(calc.)	d(obs.) − d(calc.)
CsCl	4.121	3.569	3.572	−0.003
CsBr	4.296	3.720	3.723	−0.003
CsI	4.564	3.953	3.950	0.003
$[NH_4]F$	4.438 9 *	2.709	2.709	0.000
$[NH_4]Cl$	3.875 8	3.357	3.357	0.000
$[NH_4]Br$	4.059	3.515	3.515	0.000
CaF_2	5.462	2.365	2.365	0.000
SrF_2	5.794	2.509	2.512	−0.003
$SrCl_2$	6.976 7	3.021	3.020	0.001
BaF_2	6.200 1	2.685	2.682	0.003
$BaCl_2$	7.324	3.171	3.172	−0.001

* $c_0 = 7.163\,5$.[10]

Ammonium salts. Soft-sphere radii in Table 2 for ammonium and fluoride ions are related by $M[4] = 0.971M[6]$, $M[8] = 1.033M[6]$, $X[4] = 0.971X[6]$, and $X[8] = 1.033X[6]$.

Ammonium fluoride has the wurtzite structure as a result of strong N–H ··· F hydrogen bonding.[10] The observed internuclear distance[11] is equal to the calculated distance: $d^{\frac{5}{3}} = M[4]^{\frac{5}{3}} + X[4]^{\frac{5}{3}}$; $d = 2.709$ Å. At 298 K ammonium chloride and bromide have CsCl structures as a result of weak N–H ··· X hydrogen bonding, whereas ammonium iodide has the NaCl structure.[10] The observed internuclear distances in Tables 3 and 5 agree well with the calculated distances.

Calcium fluoride structures. Soft-sphere radii for Group 2 cations with eight-co-ordination and for fluoride and chloride anions with four-co-ordination are listed in Table 2. Unit-cube dimensions for Group 2 halides with CaF_2 structures and the corresponding internuclear distances, $d = a_0 3^{\frac{1}{2}}/4$, are compared in Table 5 with distances calculated from the relation $d^{\frac{5}{3}} = M[8]^{\frac{5}{3}} + X[4]^{\frac{5}{3}}$. Differences between observed and calculated internuclear distances are ⩽0.003 Å.

Conclusions.—Metallic elements are regarded here as

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[7] Ref. 1, pp. 523—526.

[8] V. M. Goldschmidt, *Skr. Norske Vid.-Akad. Oslo*, I, *Matemat.-Naturu. Klasse*, 1926, **8**, 145.

[9] Ref. 2, p. 258.

[10] Ref. 2, p. 309.

[11] B. Morosin, *Acta Cryst.*, 1970, **B26**, 1635.

soft spherical cations held in contact without compression by electrons. Their structures resemble those of NaCl or CaF_2 if cubic close-packed cations have all octahedral (Group 1) or tetrahedral (Group 2) holes occupied by free electrons. Table 1 shows that metallic radii for twelve-co-ordination are equivalent to soft-sphere cationic radii for six- (Group 1) or eight-co-ordination (Group 2).

Internuclear distances in Groups 1 and 2 metal and ammonium halide crystals are reproduced with remarkable accuracy from soft-sphere ionic radii. Nevertheless there are anomalies: soft-sphere cations appear larger than isoelectronic soft-sphere anions; $X[4]$ appears larger than $X[6]$ for chloride; and $R[12]$ appears smaller than $M[8]$ for barium. Electron-density measurements of crystalline halides show that minima occur at distances from the metal nuclei which differ significantly from conventional ionic radii.[12]

This work is being extended to hydrides and oxides.

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[12] K. B. Harvey and G. B. Porter, ' Introduction to Physical Inorganic Chemistry,' Addison-Wesley, London, 1963, p. 25.