

Ionic radius

Ionic radius, r_{ion} , is the radius ascribed to an atom's ion. Although neither atoms nor ions have sharp boundaries, it is useful to treat them as if they are hard spheres with radii such that the sum of ionic radii of the cation and anion gives the distance between the ions in a crystal lattice. Ionic radii are typically given in units of either picometers (pm) or Angstroms (Å), with 1 Å = 100 pm. Typical values range from 30 pm (0.3 Å) to over 200 pm (2 Å).

Trends in ionic radii

X^-	NaX	AgX
F	464	492
Cl	564	555
Br	598	577

Unit cell parameters (in pm, equal to two M–X bond lengths) for sodium and silver halides. All compounds crystallize in the NaCl structure.





























Ions may be larger or smaller than the neutral atom, depending on the ion's charge. When an atom loses an electron to form a cation, the lost electron no longer contributes to shielding the other electrons from the charge of the nucleus; consequently, the other electrons are more strongly attracted to the nucleus, and the radius of the atom gets smaller. Likewise, when an electron is added to an atom, forming an anion, the added electron shields the other electrons from the nucleus, with the result that the size of the atom increases.

The ionic radius is not a fixed property of a given ion, but varies with coordination number, spin state and other parameters. Nevertheless, ionic radius values are sufficiently transferable to allow periodic trends to be recognized. As with other types

of atomic radius, ionic radii increase on descending a group. Ionic size (for the same ion) also increases with increasing coordination number, and an ion in a high-spin state will be larger than the same ion in a low-spin state. In general, ionic radius decreases with increasing positive charge and increases with increasing negative charge.

An "anomalous" ionic radius in a crystal is often a sign of significant covalent character in the bonding. No bond is *completely* ionic, and some supposedly "ionic" compounds, especially of the transition metals, are particularly covalent in character. This is illustrated by the unit cell parameters for sodium and silver halides in the table. On the basis of the fluorides, one would say that Ag^+ is larger than Na^+ , but on the basis of the chlorides and bromides the opposite appears to be true.^[1] This is because the greater covalent character of the bonds in AgCl and AgBr reduces the bond length and hence the apparent ionic radius of Ag^+ , an effect which is not present in the halides of the more electropositive sodium, nor in silver fluoride in which the fluoride ion is relatively unpolarizable.

Sizes of atoms and their ions in pm

Group 1		Group 2		Group 3		Group 16		Group 17	
Li^+  90	Li 134	Be^{2+}  59	Be 90	B^{3+}  41	B 82	O  73	O^{2-}  126	F  71	F^-  119
Na^+  116	Na 154	Mg^{2+}  86	Mg 130	Al^{3+}  68	Al 118	S  102	S^{2-}  170	Cl  99	Cl^-  167
K^+  152	K 196	Ca^{2+}  114	Ca 174	Ga^{3+}  76	Ga 126	Se  116	Se^{2-}  184	Br  114	Br^-  182
Rb^+  166	Rb 211	Sr^{2+}  132	Sr 192	In^{3+}  94	In 144	Te  135	Te^{2-}  207	I  133	I^-  206

Relative sizes of atoms and ions. The neutral atoms are colored gray, cations red, and anions blue.

9	Fluorine	F			119							22	
11	Sodium	Na				116							
12	Magnesium	Mg					86						
13	Aluminum	Al						67.5					
14	Silicon	Si							54				
15	Phosphorus	P						58		52			
16	Sulfur	S		170					51		43		
17	Chlorine	Cl			167					26 (3py)		41	
19	Potassium	K				152							
20	Calcium	Ca					114						
21	Scandium	Sc						88.5					
22	Titanium	Ti					100	81	74.5				
23	Vanadium	V					93	78	72	68			
24	Chromium	Cr					87 <i>ls</i> ; 94 <i>hs</i>	75.5	69	63	58		
25	Manganese	Mn					81 <i>ls</i> ; 97 <i>hs</i>	72 <i>ls</i> ; 78.5 <i>hs</i>	67	47 (4)	39.5 (4)	60	
26	Iron	Fe					75 <i>ls</i> ; 92 <i>hs</i>	69 <i>ls</i> ; 78.5 <i>hs</i>	72.5		39 (4)		
27	Cobalt	Co					79 <i>ls</i> ; 88.5 <i>hs</i>	68.5 <i>ls</i> ; 75 <i>hs</i>	67 <i>hs</i>				
28	Nickel	Ni					83	70 <i>ls</i> ; 74 <i>hs</i>	62 <i>ls</i>				
29	Copper	Cu				91	87	68 <i>ls</i>					
30	Zinc	Zn					88						
31	Gallium	Ga						76					
32	Germanium	Ge					87		67				
33	Arsenic	As						72		60			
34	Selenium	Se		184					64		56		
35	Bromine	Br			182			73 (4sq)		45 (3py)		53	
37	Rubidium	Rb				166							
38	Strontium	Sr					132						
39	Yttrium	Y						104					
40	Zirconium	Zr							86				
41	Niobium	Nb						86	82	78			
42	Molybdenum	Mo						83	79	75	73		
43	Technetium	Tc							78.5	74		70	
44	Ruthenium	Ru						82	76	70.5		52 (4)	50 (4)
45	Rhodium	Rh						80.5	74	69			
46	Palladium	Pd				73 (2)	100	90	75.5				
47	Silver	Ag				129	108	89					
48	Cadmium	Cd					109						
49	Indium	In						94					
50	Tin	Sn							83				

51	Antimony	Sb					90		76				
52	Tellurium	Te		207					111		70		
53	Iodine	I			206					109		67	
54	Xenon	Xe										62	
55	Caesium	Cs				181							
56	Barium	Ba					149						
57	Lanthanum	La						117.2					
58	Cerium	Ce						115	101				
59	Praseodymium	Pr						113	99				
60	Neodymium	Nd					143 (8)	112.3					
61	Promethium	Pm						111					
62	Samarium	Sm					136 (7)	109.8					
63	Europium	Eu					131	108.7					
64	Gadolinium	Gd						107.5					
65	Terbium	Tb						106.3	90				
66	Dysprosium	Dy					121	105.2					
67	Holmium	Ho						104.1					
68	Erbium	Er						103					
69	Thulium	Tm					117	102					
70	Ytterbium	Yb					116	100.8					
71	Lutetium	Lu						100.1					
72	Hafnium	Hf							85				
73	Tantalum	Ta						86	82	78			
74	Tungsten	W							80	76	74		
75	Rhenium	Re							77	72	69	67	
76	Osmium	Os							77	71.5	68.5	66.5	53 (4)
77	Iridium	Ir						82	76.5	71			
78	Platinum	Pt					94		76.5	71			
79	Gold	Au				151		99		71			
80	Mercury	Hg				133	116						
81	Thallium	Tl				164		102.5					
82	Lead	Pb					133		91.5				
83	Bismuth	Bi						117		90			
84	Polonium	Po							108		81		
85	Astatine	At										76	
87	Francium	Fr				194							
88	Radium	Ra					162 (8)						
89	Actinium	Ac						126					
90	Thorium	Th							108				

91	Protactinium	Pa						116	104	92			
92	Uranium	U						116.5	103	90	87		
93	Neptunium	Np					124	115	101	89	86	85	
94	Plutonium	Pu						114	100	88	85		
95	Americium	Am					140 (8)	111.5	99				
96	Curium	Cm						111	99				
97	Berkelium	Bk						110	97				
98	Californium	Cf						109	96.1				

Effective ionic radii in pm of elements in function of ionic charge and spin (*ls* = low spin, *hs*= high spin).

Ions are 6-coordinate unless indicated differently in parentheses (e.g. 146 (4) for 4-coordinate N^{3-}).^[6]

Number	Name	Symbol	3-	2-	1-	1+	2+	3+	4+	5+	6+	7+	8+
3	Lithium	Li				76							
4	Beryllium	Be					45						
5	Boron	B						27					
6	Carbon	C							16				
7	Nitrogen	N	146 (4)					16		13			
8	Oxygen	O		140									
9	Fluorine	F			133							8	
11	Sodium	Na				102							
12	Magnesium	Mg					72						
13	Aluminum	Al						53.5					
14	Silicon	Si							40				
15	Phosphorus	P						44		38			
16	Sulfur	S		184					37		29		
17	Chlorine	Cl			181					12 (3py)		27	
19	Potassium	K				138							
20	Calcium	Ca					100						
21	Scandium	Sc						74.5					
22	Titanium	Ti					86	67	60.5				
23	Vanadium	V					79	64	58	54			
24	Chromium	Cr					73 <i>ls</i> ; 80 <i>hs</i>	61.5	55	49	44		
25	Manganese	Mn					67 <i>ls</i> ; 83 <i>hs</i>	58 <i>ls</i> ; 64.5 <i>hs</i>	53	33 (4)	25.5 (4)	46	
26	Iron	Fe					61 <i>ls</i> ; 78 <i>hs</i>	55 <i>ls</i> ; 64.5 <i>hs</i>	58.5		25 (4)		
27	Cobalt	Co					65 <i>ls</i> ; 74.5 <i>hs</i>	54.5 <i>ls</i> ; 61 <i>hs</i>	53 <i>hs</i>				
28	Nickel	Ni					69	56 <i>ls</i> ; 60 <i>hs</i>	48 <i>ls</i>				
29	Copper	Cu				77	73	54 <i>ls</i>					

30	Zinc	Zn					74							
31	Gallium	Ga						62						
32	Germanium	Ge					73		53					
33	Arsenic	As						58		46				
34	Selenium	Se		198					50		42			
35	Bromine	Br			196			59 (4sq)		31 (3py)		39		
37	Rubidium	Rb				152								
38	Strontium	Sr					118							
39	Yttrium	Y						90						
40	Zirconium	Zr							72					
41	Niobium	Nb						72	68	64				
42	Molybdenum	Mo						69	65	61	59			
43	Technetium	Tc							64.5	60		56		
44	Ruthenium	Ru						68	62	56.5		38 (4)	36 (4)	
45	Rhodium	Rh						66.5	60	55				
46	Palladium	Pd				59 (2)	86	76	61.5					
47	Silver	Ag				115	94	75						
48	Cadmium	Cd					95							
49	Indium	In						80						
50	Tin	Sn							69					
51	Antimony	Sb						76		60				
52	Tellurium	Te		221					97		56			
53	Iodine	I			220					95		53		
54	Xenon	Xe											48	
55	Caesium	Cs				167								
56	Barium	Ba					135							
57	Lanthanum	La						103.2						
58	Cerium	Ce						101	87					
59	Praseodymium	Pr						99	85					
60	Neodymium	Nd					129 (8)	98.3						
61	Promethium	Pm						97						
62	Samarium	Sm					122 (8)	95.8						
63	Europium	Eu					117	94.7						
64	Gadolinium	Gd						93.5						
65	Terbium	Tb						92.3	76					
66	Dysprosium	Dy					107	91.2						
67	Holmium	Ho						90.1						
68	Erbium	Er						89						
69	Thulium	Tm					103	88						

70	Ytterbium	Yb					102	86.8						
71	Lutetium	Lu						86.1						
72	Hafnium	Hf							71					
73	Tantalum	Ta						72	68	64				
74	Tungsten	W							66	62	60			
75	Rhenium	Re							63	58	55	53		
76	Osmium	Os							63	57.5	54.5	52.5	39 (4)	
77	Iridium	Ir						68	62.5	57				
78	Platinum	Pt					80		62.5	57				
79	Gold	Au				137		85		57				
80	Mercury	Hg				119	102							
81	Thallium	Tl				150		88.5						
82	Lead	Pb					119		77.5					
83	Bismuth	Bi						103		76				
84	Polonium	Po							94		67			
85	Astatine	At										62		
87	Francium	Fr				180								
88	Radium	Ra					148 (8)							
89	Actinium	Ac						112						
90	Thorium	Th							94					
91	Protactinium	Pa						104	90	78				
92	Uranium	U						102.5	89	76	73			
93	Neptunium	Np					110	101	87	75	72	71		
94	Plutonium	Pu						100	86	74	71			
95	Americium	Am					126 (8)	97.5	85					
96	Curium	Cm						97	85					
97	Berkelium	Bk						96	83					
98	Californium	Cf						95	82.1					

Non-spherical Ions

The concept of ionic radii is based on the assumption of a spherical ion shape. However, from a group-theoretical point of view the assumption is only justified for ions that reside on high-symmetry crystal lattice sites like Na and Cl in halite or Zn and S in sphalerite. A clear distinction can be made, when the point symmetry group of the respective lattice site is considered,^[7] which are the cubic groups O_h and T_d in NaCl and ZnS. For ions on lower-symmetry sites significant deviations of their electron density from a spherical shape may occur. This holds in particular for ions on lattice sites of polar symmetry, which are the crystallographic point groups C_1 , C_{1h} , C_n or C_{nv} , $n = 2, 3, 4$ or 6 .^[8] A thorough analysis of the bonding geometry was recently carried out for pyrite-type disulfides, where monovalent sulfur ions reside on C_3 lattice sites. It was found that the sulfur ions have to be modeled by ellipsoids with different radii in direction of the symmetry axis and perpendicular to it.^[9] Remarkably, it turned out in this case that it is not the ionic radius, but the ionic volume that remains constant in different crystalline compounds.

References

- [1] On the basis of conventional ionic radii, Ag^+ (129 pm) is indeed larger than Na^+ (116 pm)
- [2] Landé, A. (1920). "Über die Größe der Atome" (<http://springerlink.com/content/j862631p43032333/>). *Zeitschrift für Physik* **1** (3): 191–197. . Retrieved 1 June 2011.
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