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Effective Radii of the Monovalent Coin Metals

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Abstract

Nearly all text books, tabulations, periodic systems and data banks give a rather large effective radius for Au^+ , typically 137 pm, corresponding to the order $R(\text{Cu}^+) < R(\text{Ag}^+) < R(\text{Au}^+)$. In contrast, experimental and theoretical data unanimously corroborate a *completely different smaller value*, caused by 16 pm lanthanoid contraction and 13 pm relativistic contraction, although the outer occupied $5d$ shell is relativistically expanded. In addition, small changes of the surrounding crystal structure may modify the effective radii by several pm. For coordination number $\text{CN} = 2$, $R(\text{Au}^+)$ is about 60 pm, *i.e.* definitely smaller than $R(\text{Ag}^+) \simeq 70$ pm [reference $R(\text{O}^{2-}) = 138$ pm].

Introduction

A consistent set of ionic radii of the elements can be found in the literature (Pauling, 1939; Hellwege, 1955; Cooper, 1968; Shannon & Prewitt, 1969; Shannon, 1976; Huheey, 1978; Douglas, McDaniel & Alexander, 1983; Bergerhoff, Hundt, Sievers & Brown, 1983; Fluck & Heumann, 1985; Lof, 1987; Gabe, Le Page, Charland & Lee, 1989; Lide, 1992; Bergerhoff, Kilger, Witthauer, Hundt & Sievers, 1992). According to a recent investigation among physicists (Behrens, Fricke, Luksch, Müller & Poerschke, 1993) the *CRC Handbook* (Lide, 1992) and *Landolt-Börnstein* (see Hellwege, 1955) are used as the first sources for numerical data. The values compiled in the ICSD (Bergerhoff *et al.*, 1992) for screening purposes of interatomic distances are exhibited in Fig. 1. In general the ionic radii increase in each group of the periodic system with increasing atomic number, with the exception that, as a result of the lanthanide contraction, the radii of groups 4 to 9 or 10 in row 6 are similar or even slightly smaller than in row 5 ($\text{Zr}^{4+} \simeq \text{Hf}^{4+}$, ..., $\text{Pd}^{2+} \simeq \text{Pt}^{2+}$). According to Fig. 1, however, the effective radii of the monovalent ions of group 11 and the following groups again raise monotonously; in particular $R(\text{Cu}^+) : R(\text{Ag}^+) : R(\text{Au}^+) \simeq 2 : 3 : 4$.

In contrast, all individual crystal structure determinations (see the ICSD: Bergerhoff *et al.*, 1983, 1992, and *e.g.* Sabrowsky & Hoppe, 1968; Schenk & Hoppe,

1969; Losert & Hoppe, 1985; Wagner & Hoppe, 1986, 1987*a,b*; Darriet, Devallette & Lecart, 1977; Klepp & Bronger, 1985, 1987*a,b*, 1988; Burschka & Bronger, 1977; Bronger, 1992; Baggio & Baggio, 1973; Niinistö & Larsson, 1973; Wiegiers, 1971; Janssen & Wiegiers, 1978; Takahashi, Tamaki & Sato, 1987; Jagodzinski, 1959; Johnson & Schock, 1975) of isotopic compounds of the monovalent coin metals yield interatomic distances which correspond to the radii ratio 2:3:2.5. *i.e.* distances to Au^+ are in general significantly smaller than to its lighter homologue Ag^+ , a fact which repeatedly evoked surprise.

The correct order of the radii, $R(\text{Cu}^+) < R(\text{Ag}^+) > R(\text{Au}^+)$, had already been found by Slater (1964) on the basis of empirical data. A tentative explanation of this

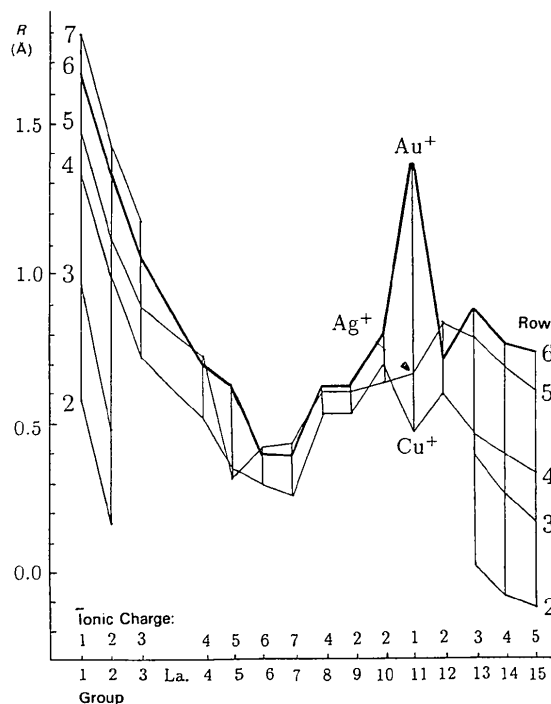


Fig. 1. Tabulated ionic radii (in Å = 100 pm) from the present update of the ICSD (Bergerhoff *et al.*, 1992) over the Periodic Table.

Table 1. *Effective ionic radii in $[XMX]^{3-}$ groups (pm) referring to $R(O^{2-}) = 138$ pm*

	M^+ (CN = 2)			O^{2-}	X^{2-} (CN = 6)		Tc^{2-}
	Cu^+	Ag^+	Au^+		S^{2-}	Se^{2-}	
Calculated from experimental interatomic distances*	49	67	61	138	168	184	205
Determined from theoretical distances (Table 2)	49	64	64	138	168	187	
Typical values from tables in the literature†	46	67	137‡	121	184	198	221

* Interatomic distances collected from the ICSD (Bergerhoff *et al.*, 1992), see also the individual references given in the *Introduction*.

† Here from the table in the ICSD (Bergerhoff *et al.*, 1992).

‡ Refers to CN = 6, not to CN = 2.

Table 2. *Interatomic distances in $[XMX]^{3-}$ groups (pm) obtained by ab initio density functional calculations*

	CuO_2^{3-}	AgO_2^{3-}	AuO_2^{3-}	CuS_2^{3-}	AgS_2^{3-}	AuS_2^{3-}	$CuSe_2^{3-}$	$AgSe_2^{3-}$	$AuSe_2^{3-}$
In vacuum	183	204	208	225	246	241	240	260	254
In Na_3AgS_2 field*	—	—	—	223	237	236	—	—	—
In Na_3AuS_2 field*	187	207	206	218	236	233	238	255	251
Experimental	184	208	204	216	237	230	238	253	241

* Madelung potential of a point-charge lattice with lattice constants as in Na_3AgS_2 or Na_3AuS_2 , respectively, and then rescaled according to the predicted internuclear distances in Na_3MX_2 .

'irregularity' may be based on the atomic calculations of Desclaux (1973) which revealed a strong relativistic contraction of *s*-valence atomic orbitals for large nuclear charges. However, a relation between the outer empty *s*-orbital radius and the radius of a closed d^{10} -shell ion only sounds reasonable if the outer *s* orbital participates in significant covalent bonding.

Calculations

Relativistically corrected density functional calculations (Baerends, 1992) of $[X-M-X]^{3-}$ groups ($M = Cu, Ag, Au$; $X = O, S, Se$) have been carried out in point-charge crystal fields of the corresponding alkali compounds. Recent corrections of Slater's $X\alpha$ density function were not applied, because they seem to work less efficiently here than for light atoms. The relativistic corrections were performed at the Dirac level for the atomic cores, by first-order perturbation theory (Schrödinger–Pauli approach) for the inner tails of the valence orbitals, and self-consistently in the outer valence shell. Polarized triple- ζ STO basis sets were used. The crystal structures needed for the crystal fields were taken from Klepp & Bronger (1985, 1987*a,b*). Further details will be published elsewhere (Liao, 1993).

The following questions will be answered:

(1) Is it possible to reproduce the experimental distances of $[X-M-X]^{3-}$ accurately by a theoretical approach?

(2) According to a reliable theory, what changes of interatomic distances are caused by: (a) the surrounding crystal structure, (b) the lanthanide contraction, and (c) relativistic effects?

(3) Is it possible to develop clear, simple rationalizations for these dependencies? Do direct relations exist between atomic orbital radii and interatomic distances?

(4) Finally we ask: How could such a discrepancy between textbook knowledge and reality historically arise in science?

Results

One can give the following definitive answers:

(1) The ICSD (Bergerhoff *et al.*, 1992; see also the individual references given in the *Introduction*) contains interatomic distances of a significant number of $[XMX]^{3-}$ compounds. These distances are representable as sums, within a few pm, of 'experimental' ionic radii as given in the first line of Table 1. $R(O^{2-}) = 138$ pm was chosen as the reference value for these radii.

The theoretical distances obtained in the present work by *ab initio* calculations agree with the experimental ones within a few pm (see Table 2). The theoretical distances are reproducible by the 'theoretical' ionic radii given in the second line of Table 1. Experimental and theoretical effective radii agree well.

The typical literature value of $R(Au^+)$ in the third line of Table 1 had originally been estimated for coordination number CN = 6, while the radii of Cu^+ and Ag^+ are usually given for CN = 2, which is quite common for group 11. Assuming a reduction of the effective radius for linear coordination (CN = 2) by about one quarter [*i.e.* $R(Au^+, CN = 2) \simeq 100$ pm], the tabulated literature values for Au^+ remain erroneous, *i.e.* larger than those of Ag^+ .

(2a) We have performed calculations of $[XMX]^{3-}$

(i) in vacuum, and in the crystal fields of

(ii) the appropriately scaled Na_3AgS_2 structure (space group *Ibam*; $[XMX]^{3-}$ is surrounded by 14 A^+ and 2 X^{2-} ions at different distances in D_{2h} symmetry, creating an anion-stabilizing potential with two minima around the two X, about 1.5 eV lower than around the M), and of

(iii) the appropriately scaled Na_3AuS_2 structure (space group *R3c*; $[XMX]^{3-}$ is rather symmetrically surrounded by 12 A^+ and 2 X^{2-} in D_{3d} symmetry, creating a nearly constant potential around the two X and the M).

The calculated $M-X$ distances depend on the surroundings (see Table 2). In most cases the crystal field causes a bond contraction, here up to 4%. ($[CuO_2]^{3-}$ is an exception; this may be an artifact of our approach, where

Table 3. *Effective ionic radii* (pm)

Ion	Pauling (1927)*	Shannon (1969, 1976)†	Typical literature values‡				This work**
			ICSD/Lide	Slater (1964)§	Shannon (1981)¶		
Cu ⁺	96	91	46/96	55	48	49	
Ag ⁺	126	129	67/126	80	71	68	
Au ⁺	137	151	137/137	55	58	62	
O ²⁻	140	126	121/132	140	(126)	138	
S ²⁻	184	170	184/184	180	170	168	
Se ²⁻	198	184	198/191	195	184	186	

* Theoretical estimates for the NaCl structure, CN = 6.

† For CN = 6.

‡ ICSD (Bergerhoff *et al.*, 1992): no reference of CN; *CRC Handbook* by Lide (1992); compare also the literature given in the *Introduction*.

§ Slater gives only one set of (atomic) radii (without CN) and argues: $R(\text{atom}) - R(\text{cation}) = R(\text{anion}) - R(\text{atom}) = \Delta$. The values in this column were obtained for $\Delta = 80$ pm.

¶ Sulfide crystal radii, CN = 2 for the metal cations, CN = 6 for the anions. Shannon gives $R(\text{Cu}^+)$ only for CN = 4; the value given above has been extrapolated.

** Recommended average of experimental and theoretical values. [If value other than $R(\text{O}^{2-}) = 138$ pm is preferred, raise $R(\text{cation})$ by δ and decrease $R(\text{anion})$ by δ .] CN = 2 for the metal cations, CN = 6 for the anions.

the solid is simulated by a small cluster imbedded in an effective potential, which may no longer be justified for the short interatomic contacts in A_3CuO_2). The two different crystal fields result in $M-X$ bond-length differences of about 2%. This is remarkable in view of the similar coordination numbers.

(2b) Lanthanide and relativistic contractions are determined by comparing the realistic model (which accounts for both 'effects'), with an artificial model where these effects are switched off. The lanthanide contraction is switched off by reducing the nuclear charge by 14 and keeping the 4f shell unoccupied (Bagus, Lee & Pitzer, 1975). Thereby the Au—S equilibrium distance in the crystal field increases by 16 pm, corresponding to a lanthanide contraction of $R(\text{Au}^+)$ from 80 to 64 pm by 20%. The lanthanide contraction for $[\text{SAuS}]^{3-}$ in vacuum is nearly twice as large. We note that the lanthanide contraction of the Au 5d atomic orbital radius is only 9 pm (Bagus *et al.*, 1975).

(2c) Upon switching off relativity, the interatomic distances of the Cu^+ , Ag^+ and Au^+ chalcogenides increase by 1.5, 4 and 13 pm, respectively. These changes are approximately proportional to Z^2 (Z = bare nuclear charge), namely $\Delta R \approx 0.002 \text{ pm} \times Z^2$. Without lanthanide and relativistic contractions and assuming that these two effects are approximately additive, $R(\text{Au}^+)$ would be nearly 50% larger and would be similar to the literature value (if drastically reduced in order to correspond to the common CN = 2). It is remarkable that the outermost 5d¹⁰ shell of Au^+ is relativistically expanded by 2 pm, while the bond length is relativistically contracted. The crystal field supports significant covalency of the $[\text{MX}_2]^{3-}$ groups, especially for the oxides, but also for the sulfides and selenides, with low Mulliken charge on the metal (0.0 to 0.2) and about 0.2 shared electrons per bond (for comparison the shared-electron number for a C—C single bond is calculated to be 0.33).

(3) Obviously there are no direct relationships between the radii of the occupied shells of individual ions and the effective ionic radii, which result from interactions of two or more atoms. The interatomic

distance results from equilibrium between attractive and repulsive forces. In addition to the ionic attraction, there is a contribution from the covalent interaction between the $p\sigma$ atomic orbital of X and the s atomic orbital of M. A relativistically contracted metal s atomic orbital may result in a relativistically contracted bond length (see, however, Schwarz, 1987). The repulsive forces result from Pauli repulsion of the closed atomic shells. A relativistically expanded d¹⁰ shell overlaps more strongly with the closed shells of the chalcogenide ions and is expected to result in stronger Pauli repulsion which is, however, partially compensated by stronger electron-nuclear attraction of the interpenetrating shells.

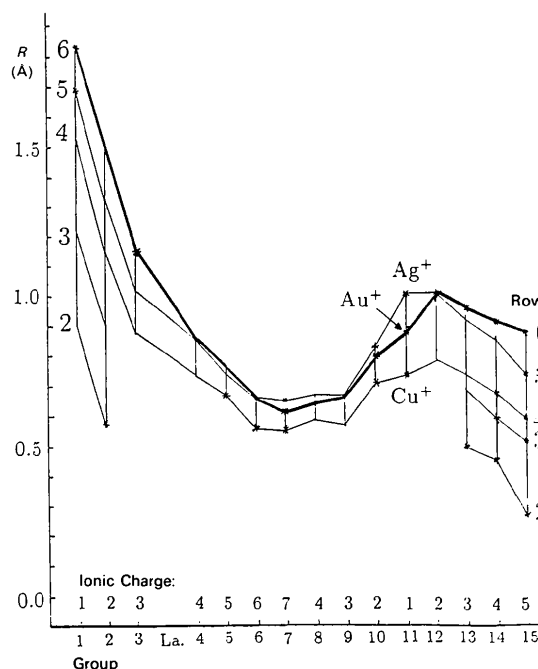


Fig. 2. Sulfide radii (in Å = 100 pm) of Shannon (1981) for CN = 6. Asterisks indicate values extrapolated to CN = 6 if not given by Shannon (1981).

In addition, as explained by Ziegler, Snijders & Baerends (1980, 1981) and Pyykkö, Snijders & Baerends (1981), the relativistic velocity-mass effect decreases the Pauli repulsion in general. According to our numerical results this latter effect is the dominant one.

(4) Pauling (1927a,b) was the first to theoretically estimate the ionic radius of Au^+ as 137 pm. At that time no one accounted for relativistic effects. Pauling also neglected the lanthanide contraction, which was erroneously considered (e.g. Cooper, 1968) to be no longer observable from group 11 onwards. Pauling's radii were explicitly estimated by him for CN = 6. They were accepted by Biltz and included in the 1931 edition of *Landolt-Börnstein* (Biltz, 1931) and in a later book (Biltz, 1934). Since then $R(\text{Au}^+) = 137$ pm [for $R(\text{O}^{2-}) = 140$; or $R(\text{Au}^+) = 151$ for $R(\text{O}^{2-}) = 126$ pm] has survived in nearly all chemical or crystallographic references (see Table 3). This is so even if the radii given for Cu^+ and Ag^+ refer to the frequent CN = 2.

Less biased by the chemical literature, Slater (1964) derived a more realistic order of the radii on an empirical basis. The correct order of radii was finally given by Shannon (1981) (Fig. 2). The latter empirical values are corroborated by our present calculations (see Table 3). Both the lanthanide contraction and the relativistic reduction of closed-shell repulsion are responsible for the change of trend of the distances in Cu^+ , Ag^+ and Au^+ compounds. Concerning the order of radii, differences between sulfide and oxide/halide radii, as well as different assumptions of the O^{2-} radius are irrelevant.

The vast secondary literature (textbooks, handbooks, data banks, tables) should be corrected according to the last two columns of Table 3.

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