

Shannon R D & Prewitt C T. Effective ionic radii in oxides and fluorides.

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Effective ionic radii were compiled from experimental interatomic distances and unit cell volumes of oxides and fluorides. These radii take into account electronic spin state and the coordination of both cations and anions and closely reproduce experimental interatomic distances in oxides and fluorides. [The SC® indicates that this paper has been cited over 1,345 times since 1969.]

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"From the outset we have been pleased with the response to our paper. The usefulness of ionic radii stems from the fact that cation coordination numbers and crystal structure types are frequently determined by the relative sizes of cations and their surrounding ligands. The radii thus allow a classification of structure types according to ionic size and, therefore, an ability to predict to some degree the crystal structures to be expected for specific compositions. Of course, the assignment of a radius to an ion may not be physically realistic in the sense that the radius corresponds to a minimum in electron density between a cation and an-ion. What we have shown is that when cation radii are added to those derived for oxide or fluoride ions, the resulting interatomic distances closely approximate the corresponding experimentally derived distances.

"The radii have been especially helpful to mineralogists who work with complex mineral phases containing many elements. For solid solutions, it has frequently been possible to get an indication of the type and valence of cations found in individual sites in a crystal from a combination of elemental analysis, interatomic distances from crystal structure refinements, and calculations of interatomic distances using the ionic radii.

"The first attempts at derivation of ionic radii were by Bragg in 1920¹ and Goldschmidt in 1926.² They

derived sets of radii from average interatomic distances in ionic and metallic crystals. Goldschmidt used $r(O^{2-}) = 1.32 \text{ \AA}$ and $r(F^-) = 1.33 \text{ \AA}$ radii which reproduced interatomic distances in both ionic and metallic crystals to an average deviation of about 0.06 Å.

"Using a more theoretical approach, Pauling³ in 1927 calculated a set of radii based on an inverse variation with effective nuclear charge in isoelectronic series of the alkali ions. The radii of the alkali ions were determined from interatomic distances of alkali halides assuming $r(O^{2-}) = 1.40 \text{ \AA}$ and $r(F^-) = 1.36 \text{ \AA}$. Subsequently, Zachariasen⁴ improved Goldschmidt's radii and Ahrens⁵ revised Pauling's radii by using ionization potentials.

"All of these sets of radii suffered from several deficiencies: (1) their sums did not accurately reproduce experimental interatomic distances, (2) they were not listed explicitly as a function of coordination number, and (3) the effects of variations in electronic spin state were not included. By the late 1960s, there existed a large quantity of crystallographic data in the form of interatomic distances and cell dimensions of iso-typic series of compounds. These data, which included over 1,000 interatomic distances in oxides and fluorides, made it possible for us to apply Goldschmidt's methods to obtain an extensive set of ionic radii. A novel feature was that we allowed anion radii to vary with CN in much the same way as cation radii vary. The variation of anion radii was small, but was sufficient to allow an excellent match between calculated and observed interatomic distances. Thus, we obtained a set of about 350 radii for cations as a function of valence, coordination, and electron spin state. Recently, this set of radii has been revised and expanded⁶ in accordance with the many crystal structure refinements which appeared between 1969 and 1975.

"It is perhaps interesting to note that the original set of radii was only meant for internal use in the solid-state chemistry program at Du Pont and was not meant to be published. It was only after Martin Buerger of MIT suggested that the radii would be useful to mineralogists and urged that they be published that we submitted our effective ionic radii paper to *Acta Crystallographica*."

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3. Pauling L. The sizes of ions and the structure of ionic crystals. *J. Amer. Chem. Soc.* 49:765-90, 1927.
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5. Ahrens L H. Use of ionization potentials. I. Ionic radii of the elements. *Cochim. Cosmochim. Acta* 2:155-69, 1952.
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