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Determination of ionic radii from cation-anion distances in crystal structures: Discussion

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ABSTRACT

It is possible to obtain values of ionic radii of Li^+, Na^+, K^+, Rb^+, F^-, Cl^-, Br^-, and I^- from the interionic distances observed in the alkali halide crystals. This statement amplifies the statement by Wondratschek (1987) that there is no way to do this with use only of the cation-anion distances.

In a paper by Wondratschek (1987) with the above title it is stated that in ionic crystals the distances between ions are provided by crystal-structure determinations but that "The radii of the ions themselves, however, are not determined by these distances. . . . For example, from the 16 alkali halides of Li, Na, K, and Rb with F, Cl, Br, and I, one obtains 16 distances. Nevertheless, there is no way to calculate the eight ionic radii from these distances." This statement suggests that the history of the determination of ionic radii from the observed distances between ions in the alkali halides be recounted.

For each of the 16 M^+X^- crystals, the M^+-M^+ and the X^--X^- distances are given by the M^+-X^- distance: they are larger by the factor $2^{1/2}$ for the NaCl structure. It was pointed out in 1920 by Landé that when $R(M^+)$ is less than $(2^{1/2} - 1)R(X^-)$, the X^- anions (as hard spheres) are in contact and determine the lattice constant. In this way he evaluated $R(I^-)$ as 2.14 Å and then evaluated the seven other ionic radii from the M^+-X^- distances in other crystals. Three years later, Wasastjerna (1923) divided the M^+-M^- contact distances in the ratio of the cube roots of the ionic volumes given by the values of the molar refraction (the electric polarizability), obtaining 2.19 Å for $R(I^-)$. In 1927, I developed a set of ionic radii with use of quantum mechanics; my value, 2.16 Å, for $R(I^-)$ is close to the values found by Landé and Wasastjerna. I also developed a theory of double repulsion that describes the smooth transition from cation-anion contact to anion-anion contact and reproduces the lattice constants more precisely (Pauling, 1928a, 1928b). All of these matters are discussed in detail in the three editions of my book *The Nature of the Chemical Bond* (1939, 1940, 1960). Discussions of the lattice constants of these crystals and of the ionic radii have also been published by several other investigators.

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