

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

HANS WONDRA SCHEK*

Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.

ABSTRACT

In ionic compounds, distances between cations and anions are equal to the sum of the ionic radii. It is proved that in such compounds, the radii cannot be calculated from the measured distances, regardless of the number of cations and anions available.

It is well known that in heterovalent compounds, the ions constituting the crystal structures can be approximated by hard spheres. The distances between the ions, i.e., the sums of the ionic radii, are provided by crystal-structure determinations. The radii of the ions themselves, however, are not determined by these distances. This is surprising because between k cations and n anions there may be $(k \times n)$ distances from which only $(k + n)$ radii are to be determined. 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.

A simple proof of this impossibility for the general case of k cations and n anions can be given in the following way. The proof uses basic theorems on the solution of linear equations only.

Each distance is the sum of two radii: $d_{pq} = r_p + r_q$, with $1 \leq p \leq k$ and $1 \leq q \leq n$. The distances form a system of $(k \times n)$ inhomogeneous linear equations for the $(k + n)$ unknown radii, from which we construct the matrix C of coefficients. The system of equations allows a unique determination of the unknown quantities if and only if the rank of C is $(k + n)$, i.e., if one of its $(k + n) \times (k + n)$ determinants is nonzero. As this matrix has $(k \times n)$ rows and $(k + n)$ columns, it can be written as shown in Table 1.

The first n lines L_1 to L_n of C are linearly independent. Only one line of the second n lines, say L_{n+1} , is independent from those before. The remaining lines L_{n+2} to L_{2n} , e.g., L_{n+i} , can be obtained from the earlier ones by linear combination: $L_{n+i} = L_{n+1} + L_i - L_1$. In the same way, from any other line set L_{pn+1} to L_{pn+n} , exactly one line is linearly independent from those before. These are n lines from the first package and $k - 1$ lines from the $k - 1$ other packages, altogether $n + k - 1$ lines. Thus, the rank

Table 1. Matrix C

100...	...00	100...00
100...	...00	010...00
100...	...00	001...00
...
100...	...00	000...10
100...	...00	000...01
010...	...00	100...00
010...	...00	010...00
010...	...00	001...00
...
010...	...00	000...10
010...	...00	000...01
001...	...00	100...00
001...	...00	010...00
.....
000...	...01	100...00
000...	...01	010...00
000...	...01	001...00
...
000...	...01	000...10
000...	...01	000...01

of the matrix is $n + k - 1$, too small to determine the $n + k$ ionic radii from the set of distances. Only the differences between the radii of the cations or between those of the anions can be calculated, not the radii themselves.

This situation changes if the distance between two cations or between two anions is included. Then from the difference and the sum of the radii, their values can be obtained. Such an approach is, however, at least questionable: In the hard-sphere model, ions of the same sign repel each other. Therefore, the distances between two cations or two anions will not reflect the sum of the radii but will be larger. On the other hand, covalent bonding forces may be involved between any two atoms and result in a distance shorter than the sum of the ionic radii.

* Permanent address: Institut für Kristallographie der Universität, Kaiserstr. 12, D-7500 Karlsruhe 1, West Germany.

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