Soft-sphere Ionic Radii for Alkali and Halogenide Ions

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The soft-sphere ionic radii of Holbrook *et al.*[1] have little obvious physical significance. A set of soft-sphere radii formulated on a sound theoretical basis[5] in 1928 gives better agreement with the experimental values for the interionic distances in alkali halogenide crystals.

IN a recently published paper[1] Holbrook, Khaled, and Smith discuss a set of soft-sphere ionic radii that they have formulated to give close agreement with the observed interionic distances in crystals. They point out that the hard-sphere ionic radii derived[2] in 1927 and discussed in successive editions of 'The Nature of the Chemical Bond,' in particular on pages 511 to 523 of the third edition,[3] when added together give radius sums that differ from the observed interionic distances in the 17 alkali halides with the sodium chloride structure at ordinary temperature and pressure by an average of 0.063 Å. Similarly poor agreement is also found with a closely similar set of radii derived empirically in 1926 by Goldschmidt.[4] Holbrook *et al.* then formulate their set of radii, chosen, together with their equation $d^k = M^k + X^k$, to give the best possible agreement with the experimental values of d, the interionic distance in the crystal; here M and X are their values of the soft-sphere radii of cations and anions, respectively, and the exponent of k is given the empirical value 5/3. The average difference between the observed and the calculated values of d for the 17 crystals is reduced from 0.065 to 0.0024 Å.

The authors do not mention, however, that in two 1928 papers[5] and on pages 523 to 530 of ref. 3, just following the pages that they quote, a set of soft-sphere radii was formulated and discussed. These radii, when used with the equations expressing the repulsive interactions between nearest pairs and next-nearest pairs of ions as well as the electrostatic interactions of all of the ions in the crystal, give agreement between observed and calculated values of d for the 17 crystals with average deviation 0.0011 Å, considerably smaller than the value 0.0024 Å obtained by Holbrook *et al.*

My soft-sphere radii for the five alkali cations and the four halogenide anions are very nearly the same as hard-sphere radii, the average difference being 0.010 Å. The reasons for the failure of additivity with the hard-sphere radii are anion contact and double repulsion. That contact of the anions, rather than of anions and cations, determines the values of the lattice constants of LiCl, LiBr, and LiI was pointed out[6] by Landé in 1920. Values of half the anion–anion distances in these crystals, 1.82, 1.95, and 2.12 Å, respectively, agree well with my hard-sphere radii of the anions, 1.81, 1.95, and 2.16 Å. Double repulsion is the combined effect of anion–anion and anion–cation repulsions.[2,3]

Both these effects are included quantitatively in my 1928 treatment of soft-sphere radii.

Both my hard-sphere radii and my soft-sphere radii were carefully defined when they were formulated in 1927 and 1928, and they have a sound theoretical basis. The theory remains essentially unchanged now; a small improvement, with little effect on numerical values, is the replacement of the Born inverse power by an exponential form for the repulsive potential.[7] So far as I can see, the radii of Holbrook *et al.* are not defined, except as values that lead to moderately good agreement with the experimental interionic distances, and they and the equation $d^k = M^k + X^k$ have no theoretical basis; indeed, the radii are incompatible with any reasonable theoretical definition in that each of the four halogenide ions is smaller than its isoelectronic alkali ion (for example F^- 1.085 Å, Na^+ 1.548 Å), instead of being larger, because of the decreased attraction of the electrons to the nucleus with the smaller electric charge (my values are F^- 1.341 Å, Na^+ 0.958 Å).

With hard-sphere ions, cation–cation contact would occur when the cations become large. The Cs–Cs distance in CsF is 4.27 Å, which is 20% less than twice the Holbrook *et al.* radius for caesium, 2.676 Å. They describe their ions as follows: 'The ions resemble soft spherical balloons with charges at the centres, so that compression occurs when ions of opposite charge are in contact.' It seems clear that compression must also occur when ions of the same sign are in contact, and hence that in every direction the size of an ion is much less than its 'radius'; thus the numbers called radii by Holbrook *et al.* have little obvious physical significance.

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REFERENCES

[1] J. B. Holbrook, F. Mahnaz Khaled, and B. C. Smith, *J.C.S. Dalton*, 1978, 1631.
[2] L. Pauling, *J. Amer. Chem. Soc.*, 1927, **49**, 765.
[3] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1960.
[4] V. M. Goldschmidt, 'Geochemische Verteilingsgesetze der Elemente,' 1926, Oslo.
[5] L. Pauling, *J. Amer. Chem. Soc.*, 1928, **50**, 1036; *Z. Krist.*, 1928, **67**, 377.
[6] A. Landé, *Z. Phys.*, 1920, **1**, 191.
[7] M. L. Huggins and J. E. Mayer, *J. Chem. Phys.*, 1933, **1**, 643.