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MADELUNG CONSTANTS AND COORDINATION

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MADELUNG CONSTANTS AND COORDINATION

David H. Templeton

July 20, 1953

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Berkeley, California

correlation for various formula types, it is necessary to use some kind of average of the coordination numbers p and q of the anions and cations. The weighted harmonic mean m , defined by the relation

$$1/m = \frac{1}{n_a + n_c} \left(\frac{n_a}{p} + \frac{n_c}{q} \right)$$

seems to be the best average for this purpose. Here n_a and n_c are the numbers of anions and cations in the molecular formula. A plot of a as a function of $1/m$, Figure 1, shows a linear relationship with an average accuracy of 0.9% for the twelve cases for which we have data. The equation of the line shown in the figure is

$$a = 1.890 - 1.000/m.$$

The values of A are taken from Sherman's review paper¹ except for Cu_2O^3 and LaCl_3 .⁴

(3) J. Sherman, Z. Krist. 87, 342 (1934).

(4) C. W. Koch, private communication.

The success of this correlation reflects the fact that the electrostatic energy is very great compared with the energy differences between various solid structures and that these differences follow a trend with coordination number. No theoretical significance is known for the linearity with $1/m$. It can be shown that the use of the harmonic mean is algebraically equivalent to using the curve to get a value of a for each atom, and then taking an arithmetical average of a for all the atoms in the substance.

This curve has already found application in predicting the Madelung constant of LaCl_3 while it was being computed by Koch, and in

again calling attention to the error in the earlier value for Cu_2O .¹ The correct value for Cu_2O , computed by Sherman,³ had escaped our attention. The curve is recommended as a check for calculated values because of the well-known pitfalls with regard to convergence and omission of terms.

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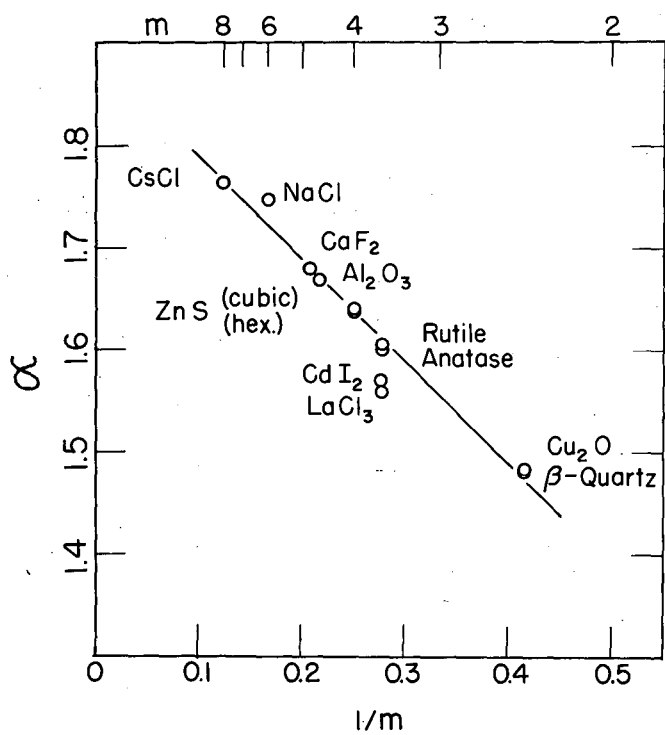


Figure 1

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Fig. 1. Plot of Madelung constant per valence bond against reciprocal of the harmonic mean coordination number.