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Interatomic Distances in Crystals of the Alkali Halides

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The constants of the empirical repulsion potential assumed by Born and Mayer between two ions, which may be termed the ionic "radii," are calculated for the alkali and halide ions from the lattice constants of the alkali

halides. By using 9 such radii the 20 lattice constants can be recalculated nearly within the probable experimental error of their determination. The good agreement is regarded as support for the assumptions involved in the calculations.

INTRODUCTION

CERTAIN equations for the lattice potential in a regular ionic lattice have been developed by Born and Mayer³ which lead to numerical values⁴ of considerable apparent accuracy. The equations imply an empirical repulsive potential between two ions which is a simple exponential function of the distance between the ionic centers and of two constants for each ion. One of these constants, that in the exponent, is assumed to have the same value for all alkali and halide ions and is determined from the compressibilities of the salts.

For any single crystal there then remain two constants, which may be called the radii of the two ions, with only the lattice constant of the crystal (the distance between the centers of closest ions) as one experimental value from which to determine them. This difficulty was not felt in the calculation of the lattice energies, since

only the *sum* of the two radii entered in any important way into the calculations and even this was not explicitly determined but eliminated from the equations with the help of the lattice constant. The lattice energies could then be computed from the lattice constant with only a very unimportant assumption concerning the difference between the radii of the two component ions.

The equations used, however, imply that the 20 lattice constants of the 20 alkali halides can be determined by the use of 9 radii, one for each of the alkali and halide ions. The purpose of this paper is to determine these 9 radii and from them recalculate the lattice constants. The excellent agreement obtained with the experimental values offers considerable support to the assumptions of the theory. Deviations from additivity of the lattice constants due to difference in structure type and in the relative sizes of the ions are quantitatively calculated.

METHOD AND RESULTS

It is assumed that the repulsive potential $b(r)$ between two ions i and j , at a distance apart r_{ij} , is given by

$$b(r) = c_{ij} b_i b_j e^{-r_{ij}/\rho} = c_{ij} b e^{(r_i + r_j - r_{ij})/\rho} \quad (1)$$

in which $\rho = 0.345 \times 10^{-8}$ cm, an empirically determined constant, b is arbitrarily chosen to have the value 10^{-12} erg, and r_i and r_j are what shall be termed the radii of the ions i and j . c_{ij} is a factor calculated by Pauling⁵ which gives the dependence of the repulsion on the charges of the ions. It has the value 1.00 for one alkali and one halide ion, 0.75 for two halide ions and 1.25 for two alkali ions, except in the cases of the lithium halides for which the values are 1.375, 0.75 and 2.00, respectively.

¹ Johnston Scholar in Chemistry.

² Most of the work here reported was carried out independently by the two authors.

³ M. Born and J. E. Mayer, *Zeits. f. Physik* **75**, 1 (1932).

⁴ J. E. Mayer and L. Helmholz, *Zeits. f. Physik* **75**, 19 (1932).

⁵ L. Pauling, *Zeits. f. Krist.* **67**, 377 (1928).

The average potential on a given ion in a crystal composed of univalent ions symmetrically surrounded, as in the NaCl and CsCl type structures, can be written

$$\Phi(r) = A(r) + B(r), \quad (2)$$

in which $A(r)$, the attractive potential, and $B(r)$, the repulsive potential, are given by the following equations:

$$A(r) = -\alpha e^2/r - C/r^6 - D/r^8, \quad (3)$$

$$B(r) = B_{+-}(r) + [B_{--}(r) + B_{++}(r)]/2, \quad (4)$$

$$B_{+-}(r) = bc_{+-} M e^{(r_+ + r_- - r)/\rho}, \quad (5)$$

$$\begin{aligned} [B_{--}(r) + B_{++}(r)]/2 &= [bc_{--} M' e^{(2r_- - ar)/\rho} + bc_{++} M' e^{(2r_+ - ar)/\rho}]/2 \\ &= bc_{+-} M e^{(r_+ + r_- - r)/\rho} [(S/a) e^{-(a-1)r/\rho}], \end{aligned} \quad (6)$$

$$S = (c_{--}/c_{+-})(M'/2M)a[1 + (c_{++}/c_{--})e^{-2\delta/\rho}]e^{\delta/\rho}. \quad (7)$$

α is Madelung's constant (1.7476 for the NaCl type, 1.7626 for the CsCl type), C and D are van der Waals constants calculated by Mayer,⁶ M and M' are the numbers of unlike and like neighbors of each ion, respectively (6 and 12 for the NaCl type, 8 and 6 for the CsCl type). a is the ratio of the distance between like neighbors to that (r) between unlike neighbors ($2\frac{1}{2}$ for the NaCl type, $2/3\frac{1}{2}$ for the CsCl type). δ is the radius difference, $r_- - r_+$.

The first derivative with respect to r is given by

$$d\Phi(r)/dr = (1/r)(\alpha e^2/r + 6C/r^6 + 8D/r^8) - (bc_{+-}M/\rho)e^{(r_+ + r_- - r)/\rho}[1 + Se^{-(a-1)r/\rho}]. \quad (8)$$

At equilibrium at zero pressure and at the absolute temperature T , $r = r_0$ and

$$r_0[d\Phi(r_0)/dr] = (3T/N\beta)(\partial V/\partial T)_P = (3T/\beta) \cdot (V/N) \cdot (1/V)(\partial V/\partial T)_P. \quad (9)$$

V/N is the molecular volume, β the coefficient of compressibility and $1/V(\partial V/\partial T)_P$ the coefficient of expansion. Combining Eqs. (8) and (9) we obtain

$$e^{(r_+ + r_-)/\rho} = e^{r_0/\rho}(\tau/r_0)/(bMc_{+-}/\rho)(1 + Se^{-(a-1)r_0/\rho}), \quad (10)$$

$$\tau = \alpha e^2/r_0 + 6C/r_0^6 + 8D/r_0^8 - (3T/N\beta)(\partial V/\partial T)_P. \quad (11)$$

By taking logarithms to the base 10,

$$(r_+ + r_-) = r_0 + 2.303\rho \log_{10}(\tau/r_0) - 2.303\rho \log_{10}(bMc_{+-}/\rho) - 2.303\rho \log_{10}(1 + Se^{-(a-1)r_0/\rho}). \quad (12)$$

All the quantities entering into the terms on the right side of this equation are known except the radius difference δ in the factor S . We can guess a first approximation for the δ values, for instance (following Born and Mayer) taking them equal to the difference between the ionic radii calculated by Goldschmidt.⁷ From the $(r_+ + r_-)$ values obtained on this assumption a

set of individual r_+ and r_- values are calculated, and from these new δ values. This process is continued until the assumed radii (Table I) give values which lead to $(r_+ + r_-)$ values consistent

TABLE I. Basic radii and repulsion constants.

	r_+ (10^{-8} cm)	b_+		r_- (10^{-8} cm)	b_-
Li ⁺	0.475	3.962			
Na ⁺	0.875	12.63	F ⁻	1.110	24.96
K ⁺	1.185	31.02	Cl ⁻	1.475	71.9
Rb ⁺	1.320	45.87	Br ⁻	1.600	103.3
Cs ⁺	1.455	67.85	I ⁻	1.785	176.6

⁶ J. Mayer, J. Chem. Phys. **1**, 270 (1933).

⁷ V. Goldschmidt, Skrifter Norske Videnskaps, Akad. Oslo, 1926, Nos. 7 and 8; Ber. d. deutsch chem. Ges. **60**, 1263 (1927).

TABLE II.

1	2 ⁸	3 ⁶	4 ⁶	5	6	7	8	9
Formula	r_0 (exp.) $\times 10^8$ cm	C $\times 10^{60}$ erg cm ⁶	D $\times 10^{76}$ erg cm ⁸	β $\times 10^{12}$ bar	$\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ $\times 10^6$ grad ⁻¹	$\frac{\alpha e^2}{r_0}$ $\times 10^{12}$ erg	$\frac{6C}{r_0^6} + \frac{8D}{r_0^8}$ $\times 10^{12}$ erg	$\frac{3T}{N\beta} \left(\frac{\partial V}{\partial T} \right)_{P=0}$ at $T = 298^\circ$ $\times 10^{12}$ erg
LiF	2.01 ₀	18	11	1.53 ⁹	9.2 ¹⁴	19.78	1.97	0.88
LiCl	2.57 ₁₆	113	104	3.41 ⁹	12.2 ¹⁴	15.46	2.78	1.09
LiBr	2.74 ₅	183	190	4.31 ⁹	14.0 ¹⁴	14.49	3.04	1.20
LiI	3.00 ₀	363	470	6.2 ¹⁰	16.7 ¹⁴	13.25	3.56	1.30
NaF	2.30 ₉₆	46	31	2.11 ¹¹	9.8 ¹⁴	17.22	2.13	1.03
NaCl	2.814	180	180	4.263 ¹²	11.0 ¹⁴	14.13	2.54	1.03
NaBr	2.98 ₁	271	300	5.08 ⁹	11.9 ¹⁴	13.34	2.71	1.11
NaI	3.23 ₁	482	630	7.0 ¹⁰	13.5 ¹⁴	12.31	2.97	1.16
KF	2.66 ₅	167	150	3.31 ⁹	10.0 ¹⁴	14.92	3.27	1.02
KCl	3.13 ₈₅	452	560	5.63 ⁹	10.1 ¹⁴	12.67	3.32	0.99
KBr	3.29 ₃	605	800	6.70 ⁹	11.0 ¹⁴	12.08	3.31	1.05
KI	3.52 ₆	924	1420	8.54 ⁹	12.5 ¹⁴	11.28	3.36	1.14
RbF	2.81 ₅	278	290	4.3 ¹⁰	10.0 ¹⁰	14.13	3.94	0.93
RbCl	3.27	691	960	6.9 ¹⁰	9.85 ¹⁴	12.16	3.97	0.89
RbBr	3.42 ₇	898	1340	7.94 ⁹	10.4 ¹⁴	11.60	3.89	0.94
RbI	3.60 ₂₆	1330	2240	9.58 ⁹	11.9 ¹⁴	10.86	3.87	1.09
CsF	3.00 ₄	495	600	4.6 ¹⁰	10.0 ¹⁰	12.23	4.77	1.06
CsCl	3.56 ₀	1530	2600	5.9 ¹³	13.65 ¹⁵	11.27	5.31	1.43
CsBr	3.71 ₃	2070	3600	7.0 ¹³	13.9 ¹⁵	10.80	5.54	1.40
CsI	3.95	2970	5800	9.3 ¹³	14.6 ¹⁵	10.15	5.48	1.33
10	11	12	13	14	15	16	17	
τ $\times 10^{12}$ erg	$\delta = r_- - r_+$ $\times 10^8$ cm	$Se^{-(a-1)r_0/\rho}$	$(r_+ + r_-)$ calc. (Eq. 12) $\times 10^8$ cm	$\delta(r_+ + r_-)$ $\times 10^8$ cm	r_0 (calc.) (Eq. 13) $\times 10^8$ cm	$\delta(r_0)$ (Col. 2-Col. 15) $\times 10^8$ cm	$\delta(r_0)$ (Eq. 14) $\times 10^8$ cm	
20.87	0.635	0.463	1.591	+0.006	2.002	+0.008	+0.008	
17.16	1.000	.643	1.960	+ .010	2.557	+ .014	+ .014	
16.33	1.125	.748	2.072	- .003	2.748	- .003	- .004	
15.51	1.310	.939	2.243	- .017	3.020	- .020	- .023	
18.32	0.235	.187	1.980	- .006	2.318	- .008	- .008	
15.64	0.600	.216	2.353	+ .003	2.810	+ .004	+ .004	
14.94	0.725	.248	2.475	.000	2.981	.000	.000	
14.11	0.910	.309	2.661	+ .001	3.229	+ .002	+ .002	
17.17	-0.075	.124	2.282	- .013	2.685	- .020	- .018	
15.00	0.290	.074	2.668	+ .008	3.127	+ .012	+ .011	
14.34	0.415	.076	2.790	+ .005	3.286	+ .007	+ .007	
13.49	0.600	.092	2.973	+ .003	3.521	+ .005	+ .005	
17.14	-0.210	.130	2.411	- .019	2.845	- .030	- .027	
15.24	0.155	.055	2.797	+ .002	3.267	+ .003	+ .003	
14.55	0.280	.052	2.923	+ .003	3.422	+ .005	+ .004	
13.63	0.465	.056	3.112	+ .007	3.653	+ .010	+ .009	
16.94	-0.345	.141	2.570	+ .004	2.996	+ .008	+ .005	
15.15	0.020	.173	2.920	- .010	3.572	- .012	- .014	
14.94	0.145	.161	3.057	+ .002	3.709	+ .004	+ .003	
14.30	0.330	.179	3.252	+ .012	3.931	+ .019	+ .017	
Average				± 0.007		± 0.010		

⁸ P. P. Ewald and C. Hermann, *Strukturbericht 1913-1928*, Akad. Verlagsgesellschaft, Leipzig, 1931.

⁹ J. C. Slater, *Phys. Rev.* **23**, 488 (1924).

¹⁰ Estimated.

¹¹ P. Bridgman, *Proc. Am. Acad.* **64**, 19 (1929).

¹² P. Bridgman, *Proc. Am. Acad.* **66**, 255 (1931).

¹³ T. W. Richards and E. P. R. Saerens, *J. Am. Chem. Soc.* **46**, 934 (1924).

¹⁴ F. A. Henglein, *Zeits. f. Elektrochem.* **31**, 424 (1925).

¹⁵ G. P. Baxter and C. F. Hawkins, *J. Am. Chem. Soc.* **38**, 266 (1916).

with the assumed radii. The close agreement is indicated by the figures in Column 14 of Table II.

The degree of agreement is very sensitive to small changes in the differences between radii of ions of the same sign. Additions or subtractions of a rather large constant to each of the negative ion radii, accompanied by subtractions or additions of the same constant to each of the positive ion radii, with further adjustment of the Li^+ radius, can be made, however, without altering the agreement markedly. We cannot claim that the radii of Table I are the *best* values but they form a consistent set; moreover all sets giving agreement with the data must have practically the same *differences* between the individual negative ion radii, also nearly the same *differences* between the individual positive ion radii, excluding Li^+ .

To recalculate r_0 from the assumed radii values of Table I, Eq. (12) is transformed to give Eq. (13).

$$r_0 - 4.606\rho \log_{10} r_0 = (r_+ + r_-) + 2.303\rho \log_{10}(bMc_{+-}/\rho) - 2.303\rho \log_{10}(r_0\tau) + 2.303\rho \log_{10}(1 + Se^{-(a-1)r_0/\rho}). \quad (13)$$

Small differences in r_0 change but slightly the last two terms (since the largest additive term of $r_0\tau$ is a constant, αe^2), hence by successive approximations values of r_0 (calc.) which satisfy the equation can be readily obtained. These are given in Column 15 of Table II. Comparison with the r_0 (exp.) values in Column 2 gives the differences in Column 16. These differences are practically within the probable error of the experimental r_0 values, hence we can consider our assumptions of an exponential repulsive potential, with constant radii and a single constant ρ to be well substantiated.

An alternative method for the calculation of

these differences is by means of the following approximate equation:

$$\delta(r_0) = \delta(r_+ + r_-) \cdot (\sigma N\beta/9V) \approx 1.4\delta(r_+ + r_-). \quad (14)$$

Values of $\delta(r_+ + r_-)$ may be taken from Column 14 of Table II; σ is defined by the equation

$$\sigma = r_0^2(\partial^2 B(r)/\partial r^2). \quad (15)$$

Its values have been calculated for the alkali halides by Born and Mayer.³ For all of them the value of the fraction $(\sigma N\beta/9V)$ is approximately 1.4. As may be seen from a comparison of Columns 16 and 17, the use of Eq. (14) with this constant value 1.4 introduces no errors greater than 0.003Å for these salts, the average error being less than 0.001Å.

In the calculation of the quantities given in Table II the figures were all carried to at least one more decimal place than there indicated so that the deviations of the $\delta(r_+ + r_-)$ values (Column 14) from zero and of the $\delta(r_0)$ values (Columns 16 and 17) from each other are not due to inaccuracies in the arithmetical computations.

Comparison of the results of the individual determinations of r_0 , as given in the *Strukturbericht*, with the r_0 (calc.) values shows that the latter agree with the experimental values well within the accuracy of the average experimental determination but not within the probable accuracy of the best determinations. Slight changes in the assumed radii might better the agreement somewhat but not a great deal.

It should be noted that the deviations from additivity of interatomic distances due to differences in sizes of the ions amount to as much as 0.14Å and deviations from additivity due to difference in structure type amount to as much as 0.10Å.