

## Lattice Energies, Equilibrium Distances, Compressibilities and Characteristic Frequencies of Alkali Halide Crystals

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possible to tell whether the reactant or the activated complex is solvated, but we feel that it is probable that it will usually be the reactant.

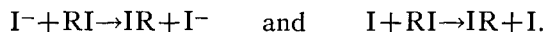
The method suggested for detecting solvation effects in unimolecular reactions, i.e., comparison of rates in various solvents, may also be extended to bimolecular reactions, and the same relations between  $E$ ,  $A$ , and  $K$ , noted above, should obtain.<sup>11</sup> The available data<sup>12</sup> is not entirely conclusive. We may call attention to the addition reaction of  $\omega$ -Br-acetophenone and aniline in various solvents. In this case it was found that the value of  $E$  is very low in benzene and chloroform as compared to various alcohols, acetone, and nitrobenzene. Corresponding to the low values of  $E$  are low values of  $A$ ; but they are *too* low and, contrary to expectations,  $K$  is very much lower in benzene and chloroform than in the other solvents. However, this reaction undoubtedly

<sup>11</sup> However, since the internal volume effect is so much more important in bimolecular reactions, its difference in different solvents may need some consideration.

<sup>12</sup> For a summary see Holtschmidt, *Zeits. f. anorg. Chemie* **200**, 82 (1931).

involves a labile bromine, and hence specific reaction with the polar solvents (possibly ionization) cannot be excluded.

Another possibility for investigating solvation effects in bimolecular reactions appears to lie in the comparison of metatheses involving respectively an atomic and the corresponding ionic reactant.<sup>13</sup> As an example we may suggest the two optical inversions



The first of these reactions should involve extensive solvation, while in most solvents the latter should not. It is to be expected that orientation and internal volume effects should be practically identical for the two reactions.

One of us (O. K. R.) wishes to acknowledge his indebtedness to the seminar of Professor A. R. Olson, which contributed greatly to the formation of his ideas concerning reactions in solution.

<sup>13</sup> In this connection see the work by Young and Olson, *J. Am. Chem. Soc.* **58**, 1157 (1936), on some ionic reactions. Note especially p. 1162.

## Lattice Energies, Equilibrium Distances, Compressibilities and Characteristic Frequencies of Alkali Halide Crystals<sup>1</sup>

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Constants in the Born and Mayer exponential expression for the repulsion between two ions have been recalculated. Using these, the lattice energies and equilibrium distances between ions have been recomputed, for alkali halide crystals. Expressions have been derived and tested for the calculation of the compressibility and the characteristic maximum infrared frequency. The relation between these two quantities is shown to be approximated by an empirical equation proposed by Madelung.

### RECALCULATION OF "a," LATTICE ENERGIES AND BASIC RADII

THE average potential energy per "molecule" in a crystal composed of univalent ions symmetrically surrounded, as in structures of the NaCl and CsCl types, can be expressed<sup>3, 4</sup>

<sup>1</sup> This paper was presented at the Pittsburgh Meeting of the American Chemical Society, September, 1936.

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

<sup>4</sup> M. L. Huggins and J. E. Mayer, *J. Chem. Phys.* **1**, 643 (1933).

by the equation

$$\Phi = -\frac{\alpha e^2}{r_0} - \frac{C}{r_0^6} - \frac{D}{r_0^8} + bc_+ Me^{a(r_+ + r_- - r_0)} + \frac{bc_- M'}{2} e^{a(2r_- - k_2 r_0)} + \frac{bc_+ M'}{2} e^{a(2r_+ - k_2 r_0)}, \quad (1)$$

where  $r_0$  = the distance between closest ion centers, obtainable from x-ray data<sup>5</sup> or from the

<sup>5</sup> P. P. Ewald and C. Hermann, *Strukturbericht 1913-1928* (Akad. Verlagsgesellschaft, Leipzig, 1931).

density;

$e$ =the electron charge ( $4.77 \times 10^{-10}$  e.s.u.)  
in the first term and the basis of  
natural logarithms elsewhere;

$C$  and  $D$ =van der Waals attraction con-  
stants;<sup>6, 7</sup>

$b$ =an arbitrary constant, taken for con-  
venience as  $10^{-12}$  erg;

$c_{+-}$ ,  $c_{--}$  and  $c_{++}$ =factors introduced<sup>8</sup> to  
allow (roughly) for the dependence  
of the repulsion between two ions on  
their charges;

$\alpha$ =Madelung's constant;

$M$  and  $M'$ =the number of nearest unlike  
and like neighbors, respectively;

$k_2$ =the ratio of the shortest distance  
between like neighbors to that ( $r_0$ )  
between unlike neighbors;

$r_+$  and  $r_-$ ="basic radii" of the positive  
and negative ions, respectively;  
( $r_+ + r_-$ ) is the equilibrium distance  
for two ions of opposite sign when  
the total attraction energy has the  
value  $-bc_{+-}$ ;

$a$  is a quantity assumed to be constant  
(i.e., independent of  $r$ ) for a given  
crystal.

Born and Mayer<sup>3</sup> computed  $a$  for the alkali  
halides from compressibility and thermal ex-  
pansion data, finding it to be roughly the same  
for all, the average value being about 2.90  
(Table III, col. 13).<sup>9</sup>

TABLE I.

1	2 LiX	3 NaX, KX, RbX, CsF	4 CsCl, CsBr, CsI
$\alpha$	1.7476	1.7476	1.7626
$c_{+-}$	1.375	1.000	1.000
$c_{++}$	2.00	1.25	1.25
$c_{--}$	0.75	0.75	0.75
$M$	6	6	8
$M'$	8	8	6
$k_2$	1.414	1.414	1.155
$k_1$	2.000	2.000	1.540

<sup>6</sup> F. London, *Zeits. f. physik. Chemie* **B11**, 222 (1930).

<sup>7</sup> J. E. Mayer, *J. Chem. Phys.* **1**, 270 (1933).

<sup>8</sup> L. Pauling, *Zeits. f. Krist.* **67**, 377 (1928).

<sup>9</sup>  $a$  is the reciprocal of the  $\rho$  used in references 3 and 4. The change from  $\rho$  to  $a$  in this paper is made to conform with the usual practice in equations for the energy of a diatomic molecule.<sup>10, 11</sup> Throughout this paper,  $a$  is given in units of  $10^8 \text{ cm}^{-1}$ .

The lattice energy of an alkali halide crystal at the absolute zero is obtained by adding to the potential energy given by Eq. (1) a term  $\epsilon = -\frac{9}{4}\nu_{\text{max}}$  for the average oscillational energy and summing over all the ions.

Using  $a = 2.90$ , Mayer and Helmholtz<sup>12</sup> calcu-  
lated lattice energies for these compounds  
(Table III, col. 16) and Huggins and Mayer<sup>4</sup>  
computed a set of basic radii (Table II, col. 2)  
from which the interionic equilibrium distances  
could be accurately calculated (Table III,  
col. 11).

Wishing to use Eq. (1) and expressions derived  
therefrom in some further work, the writer has  
recalculated  $a$  and the lattice energies. This  
seemed advisable for the following reasons:

1. In their calculations for the lithium halides,  
Born and Mayer and Mayer and Helmholtz  
used incorrect values of the coefficients  $c_{+-}$  and  
 $c_{++}$ .<sup>13</sup>

2. For  $r_+$  and  $r_-$  they used the Goldschmidt  
ionic radii, which are a poor approximation to  
the true basic radii.

3. More accurate values of compressibilities,  
coefficients of thermal expansion, van der Waals  
attraction constants and other quantities enter-  
ing into the calculations are available than those  
used before.

4. Most of the data used in the calculation of  
 $a$  are for a temperature of 298°K or thereabouts,  
rather than 273°K, the temperature used by  
Born and Mayer. (The difference in results due

TABLE II. Basic radii.

1	2 $a = 2.90$	3 $a = 3.00$
	$10^{-8} \text{ cm}$	$10^{-8} \text{ cm}$
Li <sup>+</sup>	0.475	0.570
Na <sup>+</sup>	0.875	0.940
K <sup>+</sup>	1.185	1.235
Rb <sup>+</sup>	1.320	1.370
Cs <sup>+</sup>	1.455	1.510
F <sup>-</sup>	1.110	1.050
Cl <sup>-</sup>	1.475	1.435
Br <sup>-</sup>	1.600	1.560
I <sup>-</sup>	1.785	1.750

<sup>10</sup> P. M. Morse, *Phys. Rev.* **34**, 57 (1929).

<sup>11</sup> M. L. Huggins, *J. Chem. Phys.* **3**, 473 (1935); **4**, 308 (1936).

<sup>12</sup> J. E. Mayer and L. Helmholtz, *Zeits. f. Physik* **75**, 19 (1932).

<sup>13</sup> M. Born and M. Göppert-Mayer, "Dynamische Gittertheorie der Kristalle," *Handbuch der Physik*, Vol. 24, 2nd part, second edition (1933), p. 722.

to this temperature difference is very small, however.)

The constants and experimental quantities used in the first recalculation of  $a$  are collected in Table I, column 2 of Table II, and columns 3, 5, 6 to 8, and 17 of Table III. The average  $a$  obtained was about 3.0, instead of the previous 2.9. Using this new value, the basic radii were then recalculated, the new results being given in column 3 of Table II. With these,  $a$  was once more computed for each compound, the results (Table III, column 14) differing only slightly from those obtained with the older radii.

The lattice energies computed, taking  $a = 3.00$  and using the corresponding basic radii, are compared with those of Mayer and Helmholtz and with experimental values in columns 15 to 17 of Table III.

Interionic equilibrium distances, computed with the new  $a$  and basic radii, are compared with the experimental distances and with those computed by Huggins and Mayer in columns 10 to 12 of Table III. The average deviation between the experimental values and those newly calculated is now only 0.006 Å.

#### CALCULATION OF COMPRESSIBILITIES

Born and Mayer's<sup>3</sup> Eq. (11) can be rewritten as

$$\beta = \frac{9k_1 r_0^3 F_{T,P}}{r_0^2 (d^2\Phi/dr^2)} \quad (2a)$$

with

$$F_{T,P} = 1 + \frac{T}{\beta} \left( \frac{\partial \beta}{\partial T} \right)_P + \frac{T}{\beta^2 V} \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial \beta}{\partial P} \right)_T + \frac{2T}{3V} \left( \frac{\partial V}{\partial T} \right)_P. \quad (2b)$$

$k_1$  is the molecular volume ( $V/N$ ) divided by  $r_0^3$ . (See Table I.) The denominator of Eq. (2a) is given by the expression

$$r_0^2 \frac{d^2\Phi}{dr^2} = (bc_{+-} Ma^2) r_0^2 e^{a(r_+ + r_- - r_0)} \quad (3a)$$

$$\times [1 + S(1 + k_2) e^{(1 - k_2) a r_0}] - \left[ \frac{2\alpha e^2}{r_0} + \frac{42C}{r_0^6} + \frac{72D}{r_0^8} \right]$$

with

$$S = \left( \frac{c_{--}}{c_{+-}} \right) \left( \frac{M'}{2M} \right) a \left[ 1 + \left( \frac{c_{++}}{c_{--}} \right) e^{2a(r_+ - r_-)} \right] e^{a(r_- - r_+)}. \quad (3b)$$

Calculation of  $F_{T,P}$  from the experimental quantities listed in columns 6, 7, 8 and 19 of Table III show it (column 18) to have a value within a few hundredths of 1.00 in nearly all of the compounds with which we are concerned. Hence we may write as an approximation

$$\beta \approx \frac{9k_1 r_0^3}{r_0^2 (d^2\Phi/dr^2)}. \quad (4)$$

Although the two quantities enclosed in square brackets in Eq. (3a) are by no means negligible, the error caused by the neglect of one is to a considerable extent offset by that introduced by the neglect of the other. Hence, as a further approximation, one can use the relatively simple equation

$$\beta \approx \frac{9k_1 r_0}{M} [bc_{+-} a^2 e^{a(r_+ + r_- - r_0)}]^{-1}. \quad (5)$$

The values of  $\beta$  calculation from Eqs. (2), (4) and (5) (using  $a = 3.00$  and the corresponding radii) are given in columns 20, 21 and 22 of Table III for comparison with the experimental results of column 19. The calculated values are on the whole low, yet the agreement (between columns 19 and 20) is not bad except in those cases (LiCl, LiBr, LiI, NaI, CsCl, CsBr, CsI) for which the repulsion between *like* ions is important. Perhaps Born and Mayer's assumption that the same value of  $a$  can be used for the more distant (like) atoms as for the closest (unlike) atoms is not a sufficiently good approximation, or the  $c_{+-}$ ,  $c_{++}$  and  $c_{--}$  factors introduced by Pauling may be too far off. (Certain theoretical considerations lead the writer to believe that these factors, when not equal to unity, should be considerably closer to it than assumed by Pauling.)

#### CALCULATION OF THE CHARACTERISTIC MAXIMUM FREQUENCIES

The characteristic maximum infrared frequency  $\nu_{\max}$  is customarily assumed, for an alkali halide crystal, to be the frequency of oscillation of the lattice of alkali ions, moving

TABLE III.

Formula	van der Waals Constants (Ref. 7)				$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$	$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$	$-\frac{1}{\beta} \left( \frac{\partial \beta}{\partial P} \right)_T$	$\epsilon$
	$\frac{c}{10^{-60} \text{ erg cm}^6}$	$\frac{C}{10^{-60} \text{ erg cm}^6}$	$\frac{d}{10^{-76} \text{ erg cm}^9}$	$\frac{D}{10^{-76} \text{ erg cm}^9}$	$10^{-5} \text{ deg}^{-1}$	$10^{-4} \text{ deg}^{-1}$	(Ref. 16) $10^{-12} \text{ barye}^{-1}$	$10^{-12} \text{ erg}$
LiF	0.8	18	0.6	11	9.2 <sup>15</sup>	2 <sup>18</sup>	15.3	0.14
LiCl	2.0	113	2.4	104	12.2 <sup>15</sup>	7 <sup>18</sup>	19.8	(.10)
LiBr	2.5	183	3.3	190	14.0 <sup>15</sup>	8 <sup>18</sup>	24.3	(.10)
LiI	3.3	363	5.3	470	16.7 <sup>15</sup>	(8)	37.3	(.08)
NaF	4.5	46	3.8	31	9.8 <sup>15</sup>	(2)	17.5	.11
NaCl	11.2	180	13.9	180	11.0 <sup>15</sup>	7 <sup>18</sup>	24.6	.07
NaBr	14.0	271	19.0	300	11.9 <sup>15</sup>	8 <sup>18</sup>	25.5	.06
NaI	19.1	482	31.0	630	13.5 <sup>15</sup>	(8)	40.0	.05
KF	19.5	167	21.0	150	10.0 <sup>15</sup>	1 <sup>18</sup>	20.2	(.08)
KCl	48.0	452	73.0	560	10.1 <sup>15</sup>	5 <sup>18</sup>	27.2	.06
KBr	60.0	605	99.0	800	11.0 <sup>15</sup>	6 <sup>18</sup>	31.9	.05
KI	82.0	924	156.0	1420	12.5 <sup>15</sup>	6 <sup>18</sup>	36.7	.04
RbF	31.0	278	40.0	290	(9.5)	(5)	(21.0)	(.07)
RbCl	79.0	691	134.0	960	9.85 <sup>15</sup>	7.8 <sup>16</sup>	(30.0)	.05
RbBr	99.0	898	180.0	1340	10.4 <sup>15</sup>	(8)	35.0	.04
RbI	135.0	1330	280.0	2240	11.9 <sup>15</sup>	(8)	43.0	.03
CsF	52.0	495	78.0	600	9.5 <sup>15</sup>	10.2 <sup>16</sup>	28.4	(.07)
CsCl	129.0	1530	250.0	2600	13.65 <sup>17</sup>	8.8 <sup>16</sup>	34.0	.04
CsBr	163.0	2070	340.0	3600	13.9 <sup>17</sup>	9.1 <sup>16</sup>	42.7	.03
CsI	224.0	2970	520.0	5800	14.6 <sup>17</sup>	6.8 <sup>16</sup>	49.0	(.03)

Formula	$r_0$			$a = \frac{1}{\rho}$		Lattice Energy per Mole		
	exp. (Ref. 5) $10^{-8} \text{ cm}$	H & M (Ref. 4) $10^{-8} \text{ cm}$	H $10^{-8} \text{ cm}$	B & M (Ref. 3) $10^9 \text{ cm}^{-1}$	H $10^8 \text{ cm}^{-1}$	exp. kcal.	M & H (Ref. 12) kcal.	H kcal.
LiF	2.010	2.002	2.002	2.80	3.17		240.1	243.6
LiCl	2.572	2.557	2.564	2.62	2.87		199.2	200.2
LiBr	2.745	2.748	2.741	2.62	2.74		188.3	189.5
LiI	3.000	3.020	3.013	2.17	2.41		174.1	176.1
NaF	2.310	2.318	2.314		3.09		213.4	215.4
NaCl	2.814	2.810	2.817	3.07	3.17	181.3 <sup>20</sup>	183.1	183.5
NaBr	2.981	2.981	2.981	2.99	3.15		174.6	175.5
NaI	3.231	3.229	3.230	2.60	2.74		163.9	164.3
KF	2.665	2.685	2.673	3.14	2.98		189.7	192.5
KCl	3.139	3.127	3.131	3.16	3.14		165.4	167.9
KBr	3.293	3.286	3.287	3.07	3.09		159.3	161.3
KI	3.526	3.521	3.525	2.85	2.93	153.8 <sup>21</sup>	150.8	152.4
RbF	2.815	2.845	2.837		3.09		181.6	183.0
RbCl	3.270	3.267	3.273	2.81	3.15		160.7	162.0
RbBr	3.427	3.422	3.427	2.94	3.03	151.3 <sup>20</sup>	153.5	156.1
RbI	3.663	3.653	3.663	2.85	3.01		145.3	148.0
CsF	3.004	2.996	3.004		3.68		173.7	175.7
CsCl	3.566 <sup>19</sup>	3.572	3.580	3.23	3.11		152.2	153.1
CsBr	3.713	3.709	3.712	3.06	2.94		146.3	149.6
CsI	3.95	3.931	3.936	2.82	2.76	141.5 <sup>21</sup>	139.1	142.5

as a unit, relative to the lattice of halide ions. Assuming this, we can calculate this frequency from the relation

$$\nu_{\max} = (k/4\pi^2\mu)^{1/2}, \quad (6a)$$

where  $\mu$  is related to the masses of the individual ions by the equation

$$\mu = m_+m_-/m_+ + m_- \quad (6b)$$

and  $k$  is the coefficient of  $\Delta$  (the displacement of one lattice relative to the other) in the expansion of  $d\Phi/d\Delta$  as a power series in  $\Delta$ .

For a crystal of the NaCl type, with the oscillations of the two lattices in one of the directions of the center lines between closest atoms, we can write (neglecting terms which do not vary with  $\Delta$  and considering only the 6 closest ions)

$$\begin{aligned} \Phi = & -e^2 \left[ \frac{1}{r_0 - \Delta} + \frac{1}{r_0 + \Delta} + \frac{4}{(r_0^2 + \Delta^2)^{1/2}} \right] \\ & - c \left[ \frac{1}{(r_0 - \Delta)^6} + \frac{1}{(r_0 + \Delta)^6} + \frac{4}{(r_0^2 + \Delta^2)^3} \right] \\ & - d \left[ \frac{1}{(r_0 - \Delta)^8} + \frac{1}{(r_0 + \Delta)^8} + \frac{4}{(r_0^2 + \Delta^2)^4} \right] \\ & + bc_{+-} [e^{a(r_++r_--r_0+\Delta)} + e^{a(r_++r_--r_0-\Delta)} \\ & + 4e^{a[r_++r_--(r_0^2+\Delta^2)^{1/2}}] ]. \quad (7) \end{aligned}$$

(In this equation,  $c$  and  $d$  are the van der Waals attraction constants for a single pair of unlike ions.) On differentiating, expanding in powers of  $\Delta$ , and collecting terms, one obtains

$$\begin{aligned} d\Phi/d\Delta = & [2bc_{+-}a^2(1 - 2a^{-1}r_0^{-1})e^{a(r_++r_--r_0)} \\ & - 60cr_0^{-8} - 112dr_0^{-10}]\Delta \\ & + \text{terms in higher powers of } \Delta. \quad (8) \end{aligned}$$

TABLE III.—(Continued.)

Formula	18 $F_{T,P}$	19	20	21	22	23	24	25	26 $C'$
	(Eq. 2b)	exp. (Ref. 16) $10^{-12}$ barye $^{-1}$	(Eq. 2) $10^{-12}$ barye $^{-1}$	(Eq. 4) $10^{-12}$ barye $^{-1}$	(Eq. 5) $10^{-12}$ barye $^{-1}$	exp. (Ref. 22) $10^{12}$ sec $^{-1}$	(Eq. 9) $10^{12}$ sec $^{-1}$	(Eq. 11) $10^{12}$ sec $^{-1}$	(Eq. 17) $10^8$ cm sec $^{-1}$
LiF	0.72	1.17	0.88	1.22	1.56	9.21	12.18	14.42	1.25
LiCl	1.02	3.41	2.36	2.31	3.41		9.37	9.48	1.18
LiBr	1.03	4.31	2.64	2.57	4.20		8.94	8.33	1.17
LiI	0.96	6.01	2.75	2.86	5.58		7.57	7.37	1.16
NaF	0.84	2.11	1.82	2.17	2.01	7.40	8.13	8.30	1.21
NaCl	1.06	4.263	3.95	3.72	3.58	4.91	6.17	5.76	1.17
NaBr	1.08	5.08	4.43	4.09	4.12	4.02	5.20	4.85	1.16
NaI	1.04	7.07	5.06	4.87	5.45	3.51	4.61	4.14	1.15
KF	0.87	3.30	2.69	3.10	2.77		6.70	6.61	1.18
KCl	1.03	5.63	5.67	5.53	4.25	4.25	5.06	4.66	1.15
KBr	1.05	6.70	6.58	6.29	4.89	3.40	4.12	3.71	1.14
KI	1.04	8.54	7.65	7.32	5.94	2.94	3.67	3.21	1.13
RbF	1.02	4.1	3.32	3.25	3.06		5.96	5.57	1.17
RbCl	1.12	6.65	6.55	5.85	4.38	3.54	4.35	3.79	1.14
RbBr	1.12	7.94	7.64	6.81	5.05	2.63	3.27	2.79	1.14
RbI	1.10	9.57	9.13	8.27	6.21	2.32	2.78	2.36	1.13
CsF	1.13	4.25	4.50	3.97	3.78		5.34	5.51	1.16
CsCl	1.06	5.95	4.80	4.54	4.39	2.94	3.11	3.03	1.43
CsBr	1.05	7.06	5.72	5.46	4.90	2.24	2.27	2.14	1.42
CsI	0.98	8.57	6.55	6.67	6.00		1.89	1.77	1.41

Note: Values in parenthesis are estimated.

<sup>15</sup> F. A. Henglein, *Zeits. f. Elektrochem.* **31**, 424 (1925).

<sup>16</sup> P. Bridgman, *Proc. Am. Acad.* **67**, 345 (1932).

<sup>17</sup> G. P. Baxter and C. F. Hawkins, *J. Am. Chem. Soc.* **38**, 266 (1916).

<sup>18</sup> *International Critical Tables*.

<sup>19</sup> E. Brook, I. Oftedahl and A. Pabst, *Zeits. f. physik. Chemie* **B3**, 209 (1929).

<sup>20</sup> L. Helmholtz and J. E. Mayer, *J. Chem. Phys.* **2**, 245 (1934).

<sup>21</sup> J. E. Mayer, *Zeits. f. Physik* **61**, 798 (1930). See also reference 11.

<sup>22</sup> R. B. Barnes, *Zeits. f. Physik* **75**, 723 (1932).

(The Coulomb terms exactly cancel out.)

Precisely the same equation is obtained for oscillation of the two lattices in other directions relative to each other, e.g., in the directions of a face diagonal or a body diagonal of the unit cube.

Substituting the coefficient of  $\Delta$  in Eq. (8) for  $k$  in Eq. (6a),

$$\nu_{\max} = (2\pi^2\mu)^{-\frac{1}{2}} [bc_+ a^2 (1 - 2a^{-1}r_0^{-1}) \times e^{a(r_+ + r_- - r_0)} - 30cr_0^{-8} - 56dr_0^{-10}]^{\frac{1}{2}}. \quad (9a)$$

Correspondingly, for a CsCl type crystal,

$$\nu_{\max} = (2\pi^2\mu)^{-\frac{1}{2}} [bc_+ a^2 (1 - 2a^{-1}r_0^{-1}) e^{a(r_+ + r_- - r_0)} - 40cr_0^{-8} - (224/3)dr_0^{-10}]^{\frac{1}{2}}. \quad (9b)$$

The frequencies calculated by means of these equations are compared with the experimental frequencies obtained by Barnes<sup>22</sup> in Table III, columns 23 and 24. The calculated results average about 20 percent higher than the experimental.

The van der Waals terms in Eqs. (9a) and (9b) are relatively small (in most cases less than 10 percent of the quantity from which they are subtracted), hence

$$\nu_{\max} = \left[ \frac{(1 - 2a^{-1}r_0^{-1})}{2\pi^2\mu} (bc_+ a^2 e^{a(r_+ + r_- - r_0)}) \right]^{\frac{1}{2}}. \quad (10)$$

Combining this with Eq. (5) for the compressibility gives the simple relation

$$\nu_{\max} \approx \left[ \left( \frac{9k_1(1 - 2a^{-1}r_0^{-1})}{2\pi^2 M} \right) \frac{r_0}{\mu\beta} \right]^{\frac{1}{2}}. \quad (11)$$

This has been used to compute the frequency values of column 25, Table III. The calculated quantities are about 9 percent higher than the experimental, on the average.

Madelung<sup>14</sup> has proposed, from dimensional considerations, the following relationship:

<sup>14</sup> E. Madelung, *Göttingen Nachr.* (1909), 100; (1910), 43; *Physik. Zeits.* 11, 898 (1910); M. Born and M. Göppert-Mayer, reference 13, p. 656.

$$\lambda_{\min} = C' \left[ \frac{(M_+ M_-)^{\frac{1}{2}}}{(M_+ + M_-)^2} \right]^{\frac{1}{2}} \rho^{1/6} \beta^{1/2}. \quad (12)$$

Here  $\lambda_{\min}$  is the wave-length corresponding to the maximum frequency  $\nu_{\max}$ ,  $M_+$  and  $M_-$  are the ordinary atomic weights,  $\rho$  is the density, and  $C'$  is a constant determined empirically. If we substitute

$$\lambda_{\min} = c_0 / \nu_{\max}, \quad (13)$$

$c_0$  being the velocity of light,

$$\rho = m_+ + m_- / k_1 r_0^3, \quad (14)$$

$$M_+ = N m_+, \quad (15a)$$

$$M_- = N m_-, \quad (15b)$$

$N$  being Avogadro's number, we obtain

$$\nu_{\max} = \left[ \left( \frac{c_0^2 k_1^{\frac{1}{2}}}{C'^2 N^{\frac{1}{2}}} \right) \frac{r_0}{\mu\beta} \right]^{\frac{1}{2}}. \quad (16)$$

This is obviously of the same form as Eq. (11),  $C'$  being given by

$$C' \approx \left( \frac{2^{\frac{1}{2}} \pi c_0}{3 N^{\frac{1}{2}}} \right) \left( \frac{M^{\frac{1}{2}}}{k_1^{\frac{1}{2}}} \right) (1 - 2a^{-1}r_0^{-1})^{-\frac{1}{2}}. \quad (17)$$

Although not strictly the same for different alkali halide crystals,  $C'$  does not vary greatly for those of the same structure type, as may be seen from column 26 of Table III.

## CONCLUSION

The results of the lattice energy and interionic distance calculations, using Eq. (1) with the new values of  $a$ ,  $r_+$  and  $r_-$ , are believed to be even better than those computed earlier. Taking the interactions between ions to be as assumed in the derivation of that equation, it has been shown that the compressibility and the characteristic maximum infrared frequency can be calculated with reasonable accuracy. An approximate equation relating the compressibility and this maximum frequency has been derived, tested, and shown to agree roughly with Madelung's empirical relationship.