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HIGHER ORDER ELASTIC CONSTANTS OF ALKALI HALIDES

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Abstract—The Coulomb, van der Waals and repulsive lattice sums occurring in the higher order elastic constants up to sixth order have been calculated for the rocksalt and cesium chloride structures. Numerical values of the static elastic constants up to sixth order based on a rigid ion model with van der Waals and Born–Mayer type central force interaction between first and second nearest neighbors are calculated for several alkali halides representing both structure types. Fair agreement with the available experimental third and fourth order elastic constant data is found.

1. INTRODUCTION

The analysis of experimental data of anharmonic properties is complicated by the fact that the vibrational contributions contain coupling parameters of higher order than the contributions from the cohesive energy. For example, while the cohesive contribution to the nth order elastic constants depends on the nth order coupling parameters, the vibrational contribution depends in the lowest order of the quasiharmonic approximation on the $(n+2)$nd order coupling parameters[1–4]. For alkali halides experimental data of the complete set of third order elastic (T.O.E.) constants are available for LiF[5, 6], NaF[7], NaCl[5, 8–10] and KCl[5, 8], and experimental data of the partial contractions $C_{ijklmmnn}$ of the fourth order elastic (F.O.E.) constants are available for CsCl, CsBr, CsI[11], RbCl, RbBr, RbI[12] and for NaI and KI[13]. Thus for the evaluation of the vibrational contributions to these quantities fifth and sixth order coupling parameters are required, respectively. In the long wavelength limit (continuum approximation) the vibrational contributions can be evaluated from the higher order elastic constants[14–16] without knowledge of the microscopic coupling parameters.

With such applications in mind we have calculated the static elastic constants of second through sixth order for rocksalt and cesium chloride-type alkali halides based on the rigid ion model with Coulomb, van der Waals and Born–Mayer-type central force repulsive interaction between first and second neighbors. It is the purpose of the present paper to present the lattice sums for the Coulomb, van der Waals and repulsive contributions to the second through sixth order elastic constants for the rocksalt and cesium chloride structures and to give numerical results for selected alkali halides based on the ionic radii and repulsive parameters derived for the rocksalt-type alkali halides by Tosi and Fumi[17, 18]. For the cesium halides a new set of repulsive parameters and ionic radii will be used.

Previous theoretical calculations of higher order elastic constants of alkali halides were mostly restricted to T.O.E. constants[2–4, 19–23], but for rocksalt-type alkali halides the static elastic constants through fifth order have been calculated by Nran'yan[24]. Unfortunately, the Coulomb sums in [24] were not calculated with sufficient accuracy, and several of these values are in error by several hundred per cent. Although in most of the previous work on T.O.E. constants[2–4, 20–23] thermal effects were included the results of the present paper refer to the static crystal with the room temperature value of the lattice constant, because the approximation used in the previous work[2–4, 20–23] for calculating average values of the second strain derivatives of the phonon frequencies appears to be rather crude and may even give the wrong sign for the temperature coefficients of the second order elastic constants[1, 25].

The independent higher order elastic constants have been listed up to sixth order for several of the point groups of higher symmetry, including the cubic point group O_h to which both the rocksalt and cesium chloride structures belong[26–28].

2. BASIC EQUATIONS

According to the definition of the nth order elastic constants by Brugger[29] the static values are given by

$$C_{i_1 i_2 \ldots i_{n+2}} = (1/V_c)(\partial^n \Phi / \partial \eta_{i_1 i_2} \ldots \partial \eta_{i_{n+1} i_{n+2}}) \qquad (2.1)$$

where Φ denotes the static lattice energy and V_c the volume per unit cell, and η_{ij} are the components of the Lagrangian strain tensor. If the lattice energy arises from two-body central force interactions $\phi_{\mu\nu}(R^{\bar{m}\nu})$ depending on the distance $R^{\bar{m}\nu} = |\bar{R}^{\bar{m}} - \bar{R}^{\nu}|$ of ion μ in the cell $\bar{m}$ and ion ν in the cell $\bar{m} = 0$ one obtains for centrosymmetric crystal structures by expanding the square of the distance in the strained crystal with respect to the Lagrangian strain:

$$C_{i_1 i_2 \ldots i_{n+2}} = (1/2V_c) \sum_{\bar{m},\mu,\nu} 0^n \phi_{\mu\nu}(R^{\bar{m}\nu}) X_{i_1}^{\bar{m}\nu} X_{i_2}^{\bar{m}\nu} X_{i_3}^{\bar{m}\nu} \cdots X_{i_n}^{\bar{m}\nu} X_{i_{n+1}}^{\bar{m}\nu} X_{i_{n+2}}^{\bar{m}\nu} \qquad (2.2)$$

where $0 = (1/R)(\partial/\partial R)$ and $X_i^{\bar{m}\nu}$ are the components of

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$\bar{R}^{\mu\nu}_{m\omega}$. Assuming an interatomic potential of the form

$$\phi_{\mu\nu}(R) = \pm\frac{e^2}{R} - \frac{c_{\mu\nu}}{R^6} - \frac{d_{\mu\nu}}{R^8} + b_{\mu\nu}\, e^{-R/\rho_{\mu\nu}} \tag{2.3}$$

consisting of Coulomb, van der Waals and short range repulsive interaction between first and second neighbors the nth order elastic constants for the NaCl and CsCl structures are obtained in the form:

$$C_{i_1j_1\ldots i_nj_n} = -\frac{e^2}{3V_c r}\beta(n)E_{i_1j_1\ldots i_nj_n}$$
$$-\frac{\gamma(n)}{V_c r^6}\left[c_{+-}H^U_{i_1j_1\ldots i_nj_n} + \frac{c_{++}+c_{--}}{2}H^L_{i_1j_1\ldots i_nj_n}\right]$$
$$-\frac{\delta(n)}{V_c r^8}\left[d_{+-}I^U_{i_1j_1\ldots i_nj_n} + \frac{d_{++}+d_{--}}{2}I^L_{i_1j_1\ldots i_nj_n}\right]$$
$$+\frac{1}{V_c}\zeta(n, r/\rho_{+-})Z^I_{i_1j_1\ldots i_nj_n}b_{+-}\, e^{-r/\rho_{+-}} + \frac{1}{2V_c}\zeta(n, qr/\rho_{+-})$$
$$Z^{II}_{i_1j_1\ldots i_nj_n}[b_{++}\, e^{-qr/\rho_{++}} + b_{--}\, e^{-qr/\rho_{--}}]. \tag{2.4}$$

Table 1. Factor $\zeta(n, x)$ of repulsive terms

Order n	ζ(n,x)
2	$x(x+1)$
3	$-x(x^2+3x+3)$
4	$x(x^3+6x^2+15x+15)$
5	$-x(x^4+10x^3+45x^2+105x+105)$
6	$x(x^5+15x^4+105x^3+420x^2+945x+945)$

Here r denotes the nearest neighbor distance, q the ratio of second to first neighbor distance, and

$$\beta(n) = (-1)^n(2n-1)!/2^{n-1}(n-1)! \tag{2.5a}$$
$$\gamma(n) = (-1)^n 2^{n-1}(n+2)! \tag{2.5b}$$
$$\delta(n) = (-1)^n 2^{n-1}(n+3)!/3. \tag{2.5c}$$

The factor $\zeta(n, x)$ is a polynomial in x of degree n defined by

$$\zeta(n, x) = x^{2n}\, e^x\left(\frac{1}{x}\frac{\partial}{\partial x}\right)^n e^{-x} \tag{2.6}$$

and is listed in Table 1 for $n = 2, 3, \ldots 6$.

The form of the dimensionless lattice sums indicated by the subscripted kernel letters E, H, and I is given below. In Tables 2 and 3 their values are listed for the rocksalt and cesium chloride structures in Voigt notation, replacing index pairs $ij = 11, \ldots 23, \ldots$ by single indices $\mu = 1, \ldots 4, \ldots$, and capital kernel letters by lower case letters.

Because of the central force character of the interatomic potential (2.3) the nth order elastic constants and all lattice sums are totally symmetric in all indices and obey the Cauchy relations as given in Appendix 1. In connection with the point group symmetry of O_h this leads to a total of n independent constants for $n = 2, 3, 4, 5$, and to 7 independent constants for $n = 6$.

The Coulomb sums are given by

$$E_{i_1j_1\ldots i_nj_n} = -\frac{3}{2}r\sum_{\bar{m}\mu\nu}(-1)^{\mu+\nu}\frac{X^{\mu\nu}_{i_1\bar{m}\omega}X^{\mu\nu}_{j_1\bar{m}\omega}\cdots X^{\mu\nu}_{i_n\bar{m}\omega}X^{\mu\nu}_{j_n\bar{m}\omega}}{(R^{\mu\nu}_{\bar{m}\omega})^{2n+1}}. \tag{2.7}$$

Table 2. Lattice sums for rocksalt structure

Order	$\mu\nu\ldots$	$e_{\mu\nu..}$	$h^U_{\mu\nu..}$	$h^L_{\mu\nu..}$	$i^U_{\mu\nu..}$	$i^L_{\mu\nu..}$	$z^I_{\mu\nu....}$	$z^{II}_{\mu\nu....}$
2	11	3.1386	2.0972	0.3204	2.0213	0.1376	2	2
	12	-0.6955	0.05057	0.1409	0.01363	0.06458	0	1
3	111	4.1057	2.0588	0.1822	2.0114	0.07336	2	1
	112	-0.4836	0.01918	0.06909	0.004930	0.03210	0	0.5
	123	0.2717	0.1221	0.002718	0.003766	0.0003821	0	0
4	1111	4.6123	2.0413	0.1125	2.0074	0.0412	2	0.5
	1112	-0.2536	0.008766	0.03488	0.002042	0.01609	0	0.25
	1122	-0.3209	0.006345	0.03330	0.001632	0.01588	0	0.25
	1123	0.0906	0.004069	0.0009059	0.001255	0.0001274	0	0
5	11111	4.7979	2.0316	0.07668	2.0053	0.02497	2	0.25
	11112	-0.09284	0.004858	0.01790	0.001012	0.008103	0	0.125
	11122	-0.1787	0.002506	0.01653	0.0006080	0.007924	0	0.125
	11123	0.01785	0.001403	0.0004397	0.0004223	0.00006278	0	0
	11223	0.03634	0.001121	0.0002176	0.0003480	0.00003032	0	0
6	111111	4.8011	2.0253	0.05800	2.0041	0.01678	2	0.125
	111112	-0.0015	0.003154	0.009338	0.0006031	0.004099	0	0.0625
	111122	-0.08281	0.001203	0.008307	0.0002656	0.003967	0	0.0625
	111222	-0.1089	0.0008527	0.008137	0.0002029	0.003944	0	0.0625
	111123	-0.00845	0.0005012	0.0002596	0.0001435	0.00003776	0	0
	111223	-0.01515	0.0003795	0.00008649	0.0001165	0.00001212	0	0
	112233	0.01004	0.0004318	0.00005301	0.0001377	0.000007278	0	0

Table 3. Lattice sums for cesium chloride structure

Order	$\mu\nu\ldots$	$e_{\mu\nu\ldots}$	$h^U_{\mu\nu\ldots}$	$h^L_{\mu\nu\ldots}$	$i^U_{\mu\nu\ldots}$	$i^L_{\mu\nu\ldots}$	$z^I_{\mu\nu\ldots}$	$z^{II}_{\mu\nu\ldots}$
2	11	-1.840	1.041	1.020	0.9236	0.6831	0.8889	2
	12	1.801	0.9307	0.08073	0.8978	0.02474	0.8889	0
3	111	-2.810	0.4124	0.9453	0.3233	0.6596	0.2963	2
	112	0.4851	0.3144	0.03722	0.3002	0.01172	0.2963	0
	123	0.8314	0.3019	0.006291	0.2975	0.001312	0.2963	0
4	1111	-3.330	0.1912	0.9085	0.1205	0.6482	0.09877	2
	1112	0.2596	0.1106	0.01840	0.1014	0.005737	0.09877	0
	1122	-0.0517	0.1032	0.01672	0.09958	0.005541	0.09877	0
	1123	0.2771	0.1006	0.002097	0.09915	0.0004375	0.09877	0
5	11111	-3.738	0.1079	0.8893	0.05058	0.6424	0.03292	2
	11112	0.2040	0.4162	0.009595	0.03495	0.002884	0.03292	0
	11122	-0.06500	0.03495	0.008030	0.03330	0.002699	0.03292	0
	11123	0.1206	0.03402	0.0007764	0.03317	0.0001535	0.03292	0
	11223	0.07830	0.02780	0.0005643	0.02750	0.0001197	0.03292	0
6	111111	-4.116	0.07258	0.8788	0.02542	0.6394	0.01097	2
	111112	0.1888	0.01768	0.005264	0.01258	0.001488	0.01097	0
	111122	-0.04791	0.01219	0.00410	0.01121	0.001339	0.01097	0
	111222	-0.04579	0.01163	0.003792	0.01108	0.001312	0.01097	0
	111123	0.06316	0.01175	0.0003204	0.01116	0.00005734	0.01097	0
	111223	0.02870	0.009299	0.0001964	0.009175	0.00004069	0.01097	0
	112233	0.02081	0.01104	0.0002044	0.01098	0.00004587	0.01097	0

The sum is to be extended over all unit cells $\bar{m}$, and over the values $\mu, \nu = 1, 2$. These sums were evaluated by the method of Evjen[30, 31] using seventeen successively larger neutral cubes. For the rocksalt structure they were independently calculated by Madelung's method as outlined for the T.O.E. constants by Bross[19] and as described for the higher than T.O.E. constants in Appendix 2. Agreement between the two sets of data exceeded three significant figures.

In Table 4 the Coulomb sums for the T.O.E. constants are compared with previous results of Nran'yan[3, 20], Bross[19], Blackman[32], Ghate[4] and Fuller and Naimon[33], calculated by different methods. In several cases the numerical values had to be converted to the present definition according to eqn (2.4), since Nran'yan[3, 20] and Blackman[32] present their T.O.E. constants in the notation of Birch[34]. The present results, those of Bross[19] and those of Blackman[32] and of Ghate[4] agree up to the third decimal, and the present results agree with those of Blackman[32] and Ghate[4] within a few units of the fourth decimal. The present results agree up to the last significant figure given here with the much more accurate data of Fuller and Naimon[33], which were calculated by means of the Ewald method. This should dispel the recently presented claim[35] that the Coulomb sums used by Ghate[4] are

Table 4. Comparison of Coulomb sums $e_{\alpha\beta\gamma}$ for rocksalt and cesium chloride structures from various sources with present results

		Reference			
Structure	$\alpha\beta\gamma$	Nran'yan[a]	Bross[b]	Blackman[c], Ghate[d]	Present[e]
Rocksalt	111	4.00	4.1048	4.10556	4.1057
	112	-0.500	-0.4835	-0.48345	-0.4836
	123	0.282	0.2718	0.2714	0.2717
Cesium Chloride	111	-7.21	-2.8099	-2.81061	-2.810
	112	1.21	0.4849	0.48511	0.4851
	123	0.816	0.8317	0.83138	0.8314

[a]Calculated by Evjen's method by including for rocksalt structure contributions from 4 successively larger cubes[20] and for cesium chloride structure contributions from 6 successively larger cubes[3].

[b]Calculated from Madelung's method[19].

[c]For rocksalt structure calculated by Ewald's method[32].

[d]For cesium chloride structure calculated by Evjen's method by including 11 successively larger rhombohedral parallelepipds[4].

[e]Calculated by Evjen's method by including 17 successively larger cubes.

inaccurate because of poor convergence. On the other hand, the Coulomb sums of Nran'yan[3, 20] differ significantly from the other three sets of data. As has been pointed out before by Ghate[4] this discrepancy may be attributed to the fact that in the evaluation of the Coulomb sums by Nran'yan[3, 20] by means of Evjen's method the interior of too small a number of neutral cubes was considered.

In Table 5 the Coulomb sums for the fourth and fifth order elastic constants for the rocksalt structure are compared with the corresponding values of Nran'yan[24] after conversion to the present notation according to the definition in eqn (2.4). Again it is seen that major discrepancies occur. Since the present results for the rocksalt structure were calculated independently by two different methods it is suggested that Nran'yan's values are in error because too small a number of neutral cubes was considered in the summation according to Evjen's method.

The van der Waals sums are defined as

$$H_{i_1 j_1 \ldots i_n j_n} = r^6 \sum_{\bar{m}} \frac{X^{\mu\nu}_{\bar{m}o} X^{\mu\nu}_{j_1} \cdots X^{\mu\nu}_{i_n} X^{\mu\nu}_{j_n}}{(R^{\mu\nu}_{\bar{m}o})^{2n+6}} \tag{2.8a}$$

and

$$I_{i_1 j_1 \ldots i_n j_n} = r^8 \sum_{\bar{m}} \frac{X^{\mu\nu}_{\bar{m}o} X^{\mu\nu}_{j_1} \cdots X^{\mu\nu}_{i_n} X^{\mu\nu}_{j_n}}{(R^{\mu\nu}_{\bar{m}o})^{2n+8}}. \tag{2.8b}$$

When $\mu = \nu$ the values of H and I are labelled by the superscript L, and when $\mu \neq \nu$ by U. The sums converge rapidly and were evaluated numerically by successive addition of terms until the following term contributed less than 10^{-11}.

The repulsive sums depend on the neighbor order J = I, II, ... according to

$$Z^J_{i_1 j_1 \ldots i_n j_n} = \sum_{R^{\mu\nu}_{\bar{m}o} = r_J} \frac{X^{\mu\nu}_{\bar{m}o} X^{\mu\nu}_{j_1} \ldots X^{\mu\nu}_{i_n} X^{\mu\nu}_{j_n}}{(R^{\mu\nu}_{\bar{m}o})^{2n}}. \tag{2.9}$$

where the sum has to be extended over all neighbors with a given distance r. By writing out the position vectors of the Jth neighbors of the ion at the coordinate origin these sums may be evaluated by inspection. In Tables 2 and 3 the results are given for J = I and II.

3. BORN-MAYER TYPE REPULSIVE PARAMETERS

The numerical applications were based on the Huggins–Mayer form of the pre-exponential repulsive constants as given by[36].

$$b_{\mu\nu} = b\beta_{\mu\nu}\, e^{(r_\mu + r_\nu)/\rho} \qquad (\mu, \nu = +, -). \tag{3.1}$$

Here $\beta_{\mu\nu}$ denotes the Pauling factors[36] ($\beta_{+-} = 1$, $\beta_{++} = 1.25$, $\beta_{--} = 0.75$ for the sodium, potassium and rubidium halides, and $\beta_{+-} = 1.375$, $\beta_{++} = 2.0$, $\beta_{--} = 0.75$ for the lithium halides), and r_+, r_- the ionic radii. Tosi and Fumi have derived a set of ionic radii r_+, r_- and repulsive parameters b, ρ for the seventeen rocksalt-type alkali halides based on the total interatomic potential (2.3) [17, 18]. While the parameter b is common to all alkali halides, the parameter ρ is allowed to vary from salt to salt. The ionic radii and the repulsive parameters were obtained from a simultaneous least squares fit to the experimental values for the equilibrium interionic distance and for the bulk modulus of the seventeen rocksalt-type alkali halides, with the effect of thermal motion taken into account in the approximation of Hildebrand's equation of state[17, 18]. Although, as Tosi and Fumi emphasize[17, 18], these empirical parameters are subject to the uncertainties of the experimental input data, they are frequently considered as a set of standard data and are widely used. The calculation of the higher order elastic constant data in the present paper will also be based on this set of data. The ionic radii and the repulsive parameters ρ are taken from Ref. [17], Table 1, corresponding to the first set of data with the common repulsive parameter of $b = 0.338 \times 10^{-12}$ erg/molecule. The van der Waals constants c_{+-}, c_{++}, c_{--} and d_{+-}, d_{++}, d_{--} are taken from Mayer[38].

Since under standard conditions only three alkali halides occur in the cesium chloride structure the above procedure of Tosi and Fumi for the dtermination of the repulsive parameters cannot be used for the cesium chloride-type alkali halides. Instead, we have determined a set of ionic radii and repulsive parameters from a least squares fit to the equilibrium condition, to the second order elastic constants, and to the partial contractions $\Gamma^{(3)}_{ijkl} =$

Fig. 5. Comparison of Coulomb sums $e_{\alpha\beta\gamma\delta}$ and $e_{\alpha\beta\gamma\delta\varepsilon}$ for rocksalt structure from Nran'yan[24] with present results

$\alpha\beta\gamma\delta(\varepsilon)$	Nran'yan	Present
1111	4.59	4.6123
1112	-0.449	-0.2536
1122	-0.840	-0.3209
1123	0.054	0.0906
11111	5.105	4.7979
11112	-0.054	-0.09284
11122	-0.15	-0.1787
11123	0.0301	0.01785
11223	0.0480	0.03634

Fig. 6. Ionic radii r_+ and r_- (10^{-8} cm) and repulsive parameters (10^{-12} erg/molecule) and ρ(10^{-8} cm) for cesium halides determined from least squares fit of second order elastic constants and of partial contractions of third and fourth order elastic constants. The ionic radii of Pauling[41] are listed for comparison

	Present	Pauling
r_+(Cs)	1.77	1.69
r_-(Cl)	1.74	1.81
r_-(Br)	1.85	1.95
r_-(I)	2.05	2.16
b	0.208	-
ρ	0.326	-

C_{ijklmn} and $\Gamma^{(4)}_{ijkl} = C_{ijklmnnn}$ of the T.O.E. and F.O.E. constants, respectively. To this end the function

$$\Phi = \sum_{i=1}^{3}\left(\frac{R_i - A_i}{A_i}\right)^2 + \sum_{j=1}^{9} W_j\left(\frac{X_j^{\exp} - X_j^{\text{theor}}}{X_j^{\exp}}\right)^2 \quad (3.1)$$

was minimized with respect to the six parameters r_+(Cs), r_-(Cl), r_-(Br), r_-(I), b and ρ, here assumed common to all these salts. R_i and A_i denote the repulsive and attractive parts in the equilibrium conditions, respectively,

$$R_i = b\left\{Z_1\beta_{+-}\left(\frac{r_i}{\rho}\right)\exp\left(\frac{r_+ + r_-^i - r_i}{\rho}\right) + \frac{1}{2}Z_2\left(\frac{qr_i}{\rho}\right)\left[\beta_{++}\exp\left(\frac{2r_+ - qr_i}{\rho}\right) + \beta_{--}\exp\left(\frac{2r_- - qr_i}{\rho}\right)\right]\right\} \quad (3.2a)$$

$$A_i = \frac{\alpha e^2}{r_i} + \frac{6C}{r_i^6} + \frac{8D}{r_i^8} \quad (3.2b)$$

where α is Madelung's constant, and C and D are the van der Waals constants in the expression for the lattice energy per unit cell[38]. The index i labels the three cesium chloride-type cesium halides, CsCl, CsBr and CsI. All quantities in eqns (3.2a) and (3.2b) have been defined above. The quantities $X_i (j = 1, 2, \ldots 9)$ denote the three second order elastic constants c_{11}, c_{12}, c_{44}, the three partial contractions of the T.O.E. constants $\gamma_{11}^{(3)} = c_{111} + 2c_{112}$, $\gamma_{12}^{(3)} = 2c_{112} + c_{123}$, $\gamma_{44}^{(3)} = c_{144} + 2c_{166}$, and the three partial contractions of the F.O.E. constants $\gamma_{11}^{(4)} = c_{1111} + 4c_{1112} + 2c_{1122} + 2c_{1123}$, $\gamma_{12}^{(4)} = 2c_{1112} + 2c_{1122} + 5c_{1123}$, $\gamma_{44}^{(4)} = c_{1144} + 2c_{1166} + 4c_{1244} + 2c_{1266}$. For the weight factors W_i values of 1/2, 1/4 and 1/8 have been assumed for the second order elastic constants, for the partial contractions of T.O.E. constants, and for the partial contractions of F.O.E. constants, respectively. Room temperature values were used for the experimental second, third and fourth order elastic constant data[11, 39] and for the interionic distances[40]. The results obtained from this minimization procedure are listed in Table 6. The ionic radii are seen to agree roughly with those of Pauling[41], but the cation radius of the Cs ion is 5% larger, and the anion radii are about 4–5% smaller than Pauling's values, respectively. This tendency has also been noted for the ionic radii of the ions in the rocksalt-type alkali halides[17, 18]. It should be noted, however, that because of the neglect of thermal effects in the derivation of the data in Table 6, these data cannot be considered on an equal footing with the corresponding date of Tosi and Fumi[17, 18] for the rocksalt-type alkali halides, in which thermal effects have been approximately taken into account. This may affect especially the magnitude of the pre-exponential repulsive parameter b, which is found to be about 40% smaller for the cesium chloride-type alkali halides than for the rocksalt-type halides. The hardness parameter ρ for the cesium chloride-type alkali halides is found to lie within the range of values found for the rocksalt-type alkali halides[17, 18].

4. NUMERICAL RESULTS AND DISCUSSION

The second through sixth order elastic constants were calculated from eqn (2.4) for the rocksalt-type and the cesium chloride alkali halides by using the repulsive parameters of Tosi and Fumi[17, 18] and of Table 6, respectively. For the interionic distances the room temperature values of Table 1 of Fumi and Tosi[42] and of Wyckoff[40] were used for the two structure types, respectively. In this manner that part of thermal effects which arises from thermal expansion is taken into account, but the isochoric temperature variation which arises from the strain dependence of the vibrational frequencies is omitted.

In Table 7 the individual contributions from Coulomb interaction, from the two types of van der Waals attraction, from first and second nearest neighor (1st n.n. and 2nd n.n.) repulsive interaction, and the total elastic constants of second through sixth order are listed for NaCl and CsCl. Although second and third order elastic constants have been discussed before by other authors[1–4; 19–23] they are included for completeness. As a result of the crystal symmetry reflected in the repulsive sums in Tables 2 and 3 the repulsive contributions are significantly different for the rocksalt [NaCl] and for the cesium chloride [CsCl] structure. In [NaCl] the 1st n.n. repulsive contribution, and in [CsCl] the 2nd n.n. repulsive contribution, is non-zero only if all indices are equal, i.e. for c_{11}, $c_{111}, \ldots c_{111111}$. In [NaCl] the 2nd n.n. repulsive contribution is zero if all three different coordinate indices appear, i.e. for c_{123}, $c_{1123}, \ldots c_{112233}$ and in [CsCl] the 1st n.n. contributions are equal for all elastic constants of a given order. For [NaCl] the 1st n.n. repulsive contribution (if non-zero) is always larger than the 2nd n.n. repulsive contribution, but for [CsCl] the ratio of the 2nd n.n. contributions to the 1st n.n. contribution increases rapidly with increasing order n, so that for c_{111111} the 2nd n.n. repulsive contribution is the largest, and the 1st n.n. repulsive contribution is the smallest of all individual contributions. With increasing order n the van der Waals contributions become larger and relatively more important for both structure types. For $n \geq 4$ the van der Waals contribution from the dipole–dipole interaction is comparable to or even larger than the Coulomb contribution. In general, the sign of the total nth order elastic constants is given by $(-1)^n$, with c_{123}, c_{1123}, c_{11123}, c_{11223} and c_{112233} as exceptions for NaCl and c_{11112} as the only exception for CsCl. For both structures the magnitude of the total elastic constants of a given order is considerably larger for all indices equal than for mixed indices, such as $c_{111} \gg c_{112}$, $c_{111} \gg c_{123}$, $c_{1111} \gg c_{1112}$, etc. The magnitude of the elastic constants with all indices equal increases rapidly with increasing order n (faster than 10^n). The magnitude of all other constants increases also with increasing order, but less drastically. In general, for a given set of indices the higher order elastic constants are of the same order of magnitude for both NaCl and CsCl. Exceptions are c_{1123}, c_{11123}, c_{11223}, c_{111123}, c_{111223} and c_{112233}, where because of the absence of any repulsive contribution in [NaCl] the absolute magnitude of the elastic constants for CsCl is from 7 to 32 times larger than for NaCl.

Fig. 7. Coulomb contributions, van der Waals contributions from dipole–dipole (d–d) and dipole–quadrupole (d–q) interactions, short range repulsive contributions from first and second neighbor interactions and total elastic constants of second through sixth order (in 10^{12} dyn/cm^2) for NaCl and CsCl

	Order	2		3			4				5					6						
		c_{11}	c_{12}	c_{111}	c_{112}	c_{123}	c_{1111}	c_{1112}	c_{1122}	c_{1123}	c_{11111}	c_{11112}	c_{11122}	c_{11123}	c_{11223}	c_{111111}	c_{111112}	c_{111122}	c_{111222}	c_{111123}	c_{111223}	c_{112233}
NaCl	Coulomb	-0.572	0.127	3.74	-0.44	0.25	-29.44	1.62	2.05	-0.58	275.7	-5.3	-10.3	1.0	2.1	-3,034	1	52	69	5.3	9.6	-6.3
	van der Waals (d-d)	-0.090	-0.019	0.72	0.09	0.03	-7.53	-0.55	-0.52	0.03	97.5	4.0	3.6	0.1	0.1	-1,493	-33	-29	-28	-1.2	-0.5	-0.5
	van der Waals (d-q)	-0.019	-0.003	0.20	0.02	0.00	-2.45	-0.14	-0.14	0.00	36.9	1.2	1.1	0.0	0.0	-643	-10	-10	-10	-1.4	-0.1	-0.1
	repulsive (I)	1.081	0.000	-11.89	0.00	0.00	144.97	0.00	0.00	0.00	-1,955.4	0.0	0.0	0.0	0.0	29,070	0	0	0	0.0	0.0	0.0
	repulsive (II)	0.082	0.041	-0.60	-0.30	0.00	4.75	2.38	2.38	0.00	-40.4	-20.2	-20.2	0.0	0.0	370	185	185	185	0.0	0.0	0.0
	Total	0.481	0.146	-7.83	-0.63	0.28	110.29	3.30	3.76	-0.61	-1,585.8	-20.4	-25.8	1.2	2.2	24,270	142	198	216	4.0	9.0	-6.9
CsCl	Coulomb	0.170	-0.170	-1.29	0.22	0.38	10.74	-0.84	0.17	-0.89	-108.5	5.9	-1.9	3.5	2.3	1,314	-60	15	15	-20.2	-9.2	-6.6
	van der Waals (d-d)	-0.092	-0.043	0.61	0.15	0.13	-6.03	-0.67	-0.62	-0.53	77.0	30.5	3.1	2.5	2.0	-1,179	-27	-19	-18	-13.9	-10.9	-12.9
	van der Waals (d-q)	-0.018	-0.010	0.13	0.04	0.04	-1.48	-0.19	-0.19	-0.18	21.5	1.1	1.0	1.0	0.8	-372	-7	-7	-7	-5.9	-4.8	-5.8
	repulsive (I)	0.286	0.286	-1.24	-1.24	-1.24	5.88	5.88	5.88	5.88	-30.3	-30.3	-30.3	-30.3	-30.3	169	169	169	169	169.3	169.3	169.3
	repulsive (II)	0.161	0.000	-2.37	0.00	0.00	37.53	0.00	0.00	0.00	-641.3	0.0	0.0	0.0	0.0	11,779	0	0	0	0.0	0.0	0.0
	Total	0.506	0.066	-4.15	-0.83	-0.69	46.64	4.18	5.24	4.28	-681.5	+7.2	-28.0	-23.3	-25.2	11,712	75	159	159	129.4	144.4	144.0

Table 8. Calculated quasi-static elastic constants of second through sixth order (in 10^{12} dyn/cm^2) of selected alkali halides

Order	2		3			4				5					6						
	c_{11}	c_{12}	c_{111}	c_{112}	c_{123}	c_{1111}	c_{1112}	c_{1122}	c_{1123}	c_{11111}	c_{11112}	c_{11122}	c_{11123}	c_{11223}	c_{111111}	c_{111112}	c_{111122}	c_{111222}	c_{111123}	c_{111223}	c_{112233}
LiF	0.735	0.617	-10.73	-2.49	1.00	133.0	11.40	13.10	-2.28	-1,670	-56.1	-76.1	4.3	8.2	22,600	267	476	542	17.5	-33.2	-25.4
LiCl	0.351	0.258	-5.53	-1.17	0.38	71.9	6.22	6.90	-0.88	-952	-37.3	-45.2	1.7	3.2	13,500	241	324	350	5.4	-12.9	-9.8
NaF	0.417	0.345	-6.51	-1.39	0.62	82.2	6.40	7.38	-1.31	-1,040	-32.2	-43.6	2.5	4.7	13,900	161	280	317	10.0	-19.2	-14.8
NaCl	0.481	0.146	-7.83	-0.63	0.28	110.3	3.30	3.76	-0.61	-1,586	-20.4	-25.8	1.2	2.2	24,270	142	198	216	4.0	9.0	-6.9
KF	0.358	0.208	-5.68	-0.92	0.39	74.6	4.76	5.33	-0.76	-985	-28.4	-35.0	1.5	2.8	13,700	185	255	276	5.0	-11.2	-8.8
KCl	0.321	0.086	-5.60	-0.35	0.21	82.1	1.67	1.97	-0.40	-1,215	-9.5	-12.9	0.8	1.5	19,012	59	96	833	2.4	5.6	-4.7
RbCl	0.350	0.068	-6.45	-0.28	0.19	101.0	1.34	1.60	-0.34	-1,580	-8.0	-11.0	0.7	1.2	26,300	55	87	96	1.9	-5.1	-4.1
CsCl	0.506	0.066	-4.15	-0.83	-0.69	46.6	4.18	5.24	4.28	-682	+7.2	-28.0	-23.3	-25.2	11,712	75	159	159	129.4	144.4	144.0
CsI	0.337	0.055	-2.92	-0.68	-0.59	35.0	3.75	4.46	3.84	-553	-1.3	-25.5	-22.5	-23.7	10,274	97	154	154	135.0	145.1	144.8

In Table 8 the total elastic constants are listed for seven representative rocksalt-type alkali halides and for two cesium halides. While there is very little difference between the data for the two cesium halides, variations up to a factor of 9 occur among the rocksalt-type alkali halides. This results partly from differences in lattice constant, and partly from different ionic radii.

For those four alkali halides, for which experimental data on the complete set of T.O.E. constants are available, the calculated and experimental second and third order elastic constants are compared in Table 9. Also included are theoretical values based on four different versions of the rigid ion model [4, 20, 21, 23]. In Nran'yan's model [20] van der Waals forces and 2nd n.n. interaction are neglected, and in Ghate's model [4] van der Waals interaction is neglected. In both the models by Ghate [4] and by Paul [23] a Born repulsive potential with the same pre-exponential factor for 1st and 2nd n.n. interaction is used, thereby neglecting the ionic size effect included in the Huggins–Mayer form according to eqn (3.1). The model of Lincoln *et al.* [21] is based on the interaction potential (2.3) with the Huggins–Mayer form (3.1) for the pre-exponential factor, but the Pauling factors β_{++} and β_{--} were inadvertently interchanged. In the data of Paul [23] three-body type short range interactions arising from the deformability of the electron distribution of the ions have been included on the basis of a model proposed by Basu and Sengupta [43] and Sarkar and Sengupta [44, 45]. For the repulsive parameters mostly values from Tosi [18] have been used [4, 21], but Nran'yan's values [20] are based on assumed values of the hardness parameter $\rho (0.333 \times 10^{-8}$ cm, except for LiF, for which the value 0.250×10^{-8} cm is used), and the pre-exponential factor of the repulsive potential is determined from the equilibrium condition, with the interionic distance referred to the static crystal [20]. For NaCl and NaF the repulsive parameters used by Paul [23] were determined from the static values of the bulk modulus and interionic distance, and the three-body force constant was determined from the static value of the Cauchy difference $c_{12} - c_{44}$. All four sets of data [4, 20, 21, 23] refer to room temperature, and thermal effects are calculated in the Einstein approximation, with Born's value of $\langle \omega^2 \rangle^{1/2}$ for the average phonon frequency. The model of Lincoln *et al.* [21] agrees closest with the model used in the present paper. Except for the interchanged values of β_{++} and β_{--} the interatomic potential and repulsive parameters of Ref. [21] are identical with those used here, and the main difference consists in the more elaborate calculation of thermal effects in Ref. [21].

For the second order elastic constants the present model gives values which in some cases differ considerably from the experimental values, especially for c_{11} for LiF and NaF. For NaCl and KCl the discrepancy for the model of Lincoln *et al.* [21] is larger than for the present model, although in the former model thermal effects are treated more adequately than in the present model. It can also be seen that for the T.O.E. constants the discrepancy expressed in per cent is smaller than for the second order elastic constants. A possible explanation for this is that many body effects and/or thermal effects are more pronounced for the second than for the third order elastic constants. Another possibility is that for LiF and NaF with the largest discrepancies for both second and third order elastic constants the ionic radii and repulsive parameters of Fumi and Tosi [17, 18] are less reliable than for NaCl and KCl.

Inspection of Table 9 shows that in most cases the experimental T.O.E. constant data of different authors agree to within a few per cent, but with discrepancies larger than the experimental errors given. However, some data show larger deviations and are either less plausible than the data of other authors (c_{111} for LiF and c_{112} for NaCl), or are more isolated from the group of data of the other three authors (c_{123}, c_{144} and c_{456} for NaCl). Some of the theoretical data of different authors exhibit large differences, which are especially pronounced in the case of c_{111} for LiF and NaF. For c_{144} and c_{456} all, and for c_{166}, most theoretical data agree within a few per cent. Therefore evaluation of the theoretical models on the basis of their agreement with experimental data should focus mostly on the constants c_{111}, c_{112} and c_{123}.

Comparison of the various theoretical T.O.E. constant values with the experimental data does not reveal a clear pattern of superiority for any of the theoretical models. For c_{111} Ghate's model [4] gives the best or second best agreement. For NaF and KCl Paul's model [23] gives somewhat better agreement. Thus inclusion of three body forces in that model appears to be a step in the right direction, but for NaF the magnitude of the effect is overestimated. On the other hand for c_{112} and c_{123} in NaF the model of Paul gives the largest discrepancy. For c_{111} the present model gives better agreement than those of Nran'yan [20] and Lincoln *et al.* [21]. For Ghate's model the discrepancies for c_{111} range from 1% (NaCl) to 42% (NaF), whereas for the present model the discrepancies range from 9% (NaCl) to 56% (NaF). For LiF and NaF Ghate's model and the present model give the best and equally good agreement for c_{112}. In several other cases the present model gives the best agreement (c_{123} for LiF and NaCl). It is surprising that the improved models of Lincoln *et al.* [21] and of Paul [23] give less satisfactory agreement than the original model of Ghate [4]. Although in the present model thermal effects are only partly and approximately included the overall agreement with the experimental data is comparable to that for other models. This provides some justification for presenting here the higher than T.O.E. constants up to sixth order calculated from this model. Improved theoretical calculations should include many body effects and an improved method for evaluating the mode average in the treatment of thermal effects. The success of the anisotropic continuum approximation in accounting for the temperature coefficients of the second order elastic constants [14–16] suggests that extension of this model to the temperature variation of the T.O.E. and F.O.E. constants may be a more promising approach than Born's approximation of replacing the mode average $\langle \omega \rangle$ by $\langle \omega^2 \rangle^{1/2}$ [1]. In addition, deviations from the simple exponential dependence on interionic distance in the Born–Mayer potential will become more pronounced with

Table 9. Comparison of experimental and theoretical second and third order elastic constants (10^{12} dyn/cm^2) at 300°K

Material		Reference	c_{11}	c_{12}	c_{44}	c_{111}	c_{112}	c_{123}	c_{144}	c_{166}	c_{456}
LiF	Exp.	a	1.140	0.477	0.636	-14.2 ± 0.3	-2.6 ± 0.2	1.5 ± 0.3	0.85 ± 0.10	-2.73 ± 0.13	0.94 ± 0.06
		b				-6.9 ± 0.6					
	Theor.	Present	0.735	0.617	0.617	-10.73	-2.49	1.00	1.00	-2.49	1.00
		c				-22.3	-1.9	0.87	1.00	-1.78	1.00
		d				-13.5	-2.50	0.88	0.98	-2.54	0.96
NaF	Exp.	e	0.963	0.242	0.276	-14.8 ± 0.8	-2.7 ± 0.4	2.8 ± 0.6	0.46 ± 0.06	-1.14 ± 0.03	0.00 ± 0.01
	Theor.	Present	0.417	0.345	0.345	-6.51	-1.39	0.62	0.62	-1.39	0.62
		c				-7.98	-1.06	1.02	0.57	-1.00	0.57
		d				-8.56	-1.39	0.49	0.56	-1.43	0.54
		f				-19.83	-0.65	0.23	0.56	-1.36	0.59
NaCl	Exp.	a	0.494	0.127	0.128	-8.4 ± 0.3	-0.50 ± 0.07	0.46 ± 0.09	0.29 ± 0.05	-0.60 ± 0.04	0.26 ± 0.01
		g	0.493	0.129	0.128	-8.8	-0.57	0.28	0.26 ± 0.02	-0.61 ± 0.01	0.27 ± 0.01
		h	0.498	0.130	0.128	-8.23 ± 0.02	0.02 ± 0.05	0.53 ± 0.07	0 23 ± 0.03	-0.61 ± 0.03	0.20 ± 0.01
		i	0.496	0.131	0.128	-8.6 ± 0.08	-0.50 ± 0.04	0.09 ± 0.08	0.07 ± 0.03	-0.59 ± 0.01	0.13 ± 0.02
	Theor.	Present	0.481	0.146	0.146	-7.83	-0.63	0.28	0.28	-0.63	0.28
		c				-5.8	-0.51	0.20	0.27	-0.47	0.27
		d				-8.61	-0.52	0.16	0.26	-0.57	0.25
		j	0.358	0.098	0.123	-7.36	-0.53	0.13	0.27	-0.61	0.25
		f				-8.70	-0.68	0.09	0.27	-0.85	0.27
KCl	Exp.	a	0.409	0.0704	0.063	-7.3 ± 0.4	-0.24 ± 0.04	0.11 ± 0.04	0.23 ± 0.04	-0.26 ± 0.02	0.16 ± 0.01
		g	0.408	0.0705	0.063	-7.0	-0.22	0.13	0.13 ± 0.01	-0.245 ± 0.002	0.118 ± 0.004
	Theor.	Present	0.321	0.086	0.086	-5.60	-0.35	0.21	0.21	-0.35	0.21
		c				-5.3	-0.34	0.10	0.16	-0.30	0.16
		d				-6.01	-0.32	0.09	0.16	-0.36	0.16
		j	0.218	0.054	0.074	-5.46	-0.27	0.06	0.17	-0.33	0.16
		f				-6.59	-0.26	0.03	0.17	-0.42	0.17

[a]Drabble and Strathen[5]; [c]Bensch[7]; [b]Gluyas[9]; [b]Archer *et al.*[6]; [f]Paul[23]; [i]Swartz[10]; [e]Nran'yan[20]; [g]Chang[8]; [j]Lincoln *et al.*[21]; [d]Ghate[4].

Experimental second order elastic constants are adiabatic values, third order elastic constants intermediate adiabatic-isothermal quantities. Theoretical values are isothermal quantities, except for present results, which refer to a static crystal with room temperature value of the interionic distance.

increasing order of the elastic constants, especially for c_{111} with its dominating 1st n.n. repulsive contribution.

While no experimental data on individual F.O.E. constants of alkali halides are available, for three alkali halides numerical values of c_{1111} and c_{1112} have been deduced by Garber and Granato from the temperature coefficients of the second order elastic constants[16]. Their values are based on theoretical expressions for the mode averages of the second strain derivatives of the phonon frequencies derived in the anisotropic elastic continuum approximation[14, 15]. In addition, the Cauchy relations have been assumed, and the number of independent F.O.E. constants has been reduced from 4 to 2 through the assumptions[16]

$$c_{1112} = c_{11222} \tag{4.1a}$$

and

$$c_{1123} = 0. \tag{4.1b}$$

These two relations are valid if only 1st and 2nd n.n. repulsive forces are present. As the data in Table 8 indicate the deviations from eqn (4.1a) do not exceed about 20%, and c_{1123} is always smaller than about 25% of c_{1112}. Thus the two approximations (4.1a) and (4.1b) are fairly well justified. Comparison of the present F.O.E. constants with those of Garber and Granato[16] in Table 10 shows excellent agreement for c_{1111} for KCl, fair agreement for both c_{1111} and c_{1112} for RbF, and larger discrepancies for the remaining constants, especially for c_{1112} for LiBr. The discrepancies may be partly due to the limitations of the anisotropic continuum model, i.e. neglect of dispersion and of the optical branches of the phonon dispersion relations. However, the fair to good agreement obtained for some cases, especially for c_{1111}, seems to suggest that the theoretical data presented here are in error, especially for LiBr. The most plausible reason for this is the uncertainty of the individual repulsive parameters ρ and of the ionic radii of Tosi and Fumi[17, 18] which are based on experimental data of the bulk modulus, its temperature and pressure coefficient, of the lattice constant and of the thermal expansion coefficient. This suggestion is supported by the fact that

Table 10. Comparison of fourth order elastic constants (in 10^{12} dyn/cm^2) calculated from rigid ion model with values of Garber and Granato[16] calculated from temperature dependence of second order elastic constants

		c_{1111}	c_{1112}
LiBr	Present	62.2	5.65
	Ref [16]	120.0	0.354
KCl	Present	82.1	1.67
	Ref [16]	82.8	0.559
RbF	Present	87.0	4.66
	Ref [16]	66.0	3.1

the deviation of the calculated lattice energy from the experimental value is largest for LiBr (3.5 kcal/mole) and smallest for KCl (0.1 kcal/mole). In addition, the F.O.E. constant data of Garber and Granato[16] may be in error because they are based on T.O.E. constant data as input, and because for LiBr and RbF theoretical values of Ghate[4] have been used for this purpose. These T.O.E. constant values give pressure coefficients of the second order elastic constants which are for LiBr and RbF in poor agreement with experimental data[46, 47]. Other conceivable reasons for the discrepancy should be of minor influence, such as the neglect of non-central force and many-body type short range interactions by both Garber and Granato[16] and by the present authors, and the fact that the values of Ref. [16] refer to the static crystal, whereas the present results refer to 300°K and partly include thermal effects.

Experimental data for the first pressure derivatives of the elastic constants which are equivalent to the partial contractions C_{ijklmn} are available for all alkali halides. They have been discussed for the rocksalt-type alkali halides by Smith and collaborators[46, 48, 49] in the context of the Born model. For RbCl, RbBr, RbI, NaI and KI the second pressure derivatives of the second order elastic constants, which are equivalent to the partial contractions $C_{ijklmnn}$ of the F.O.E. constants have been measured and shown to agree quite well with theoretical data based on the Huggins–Mayer form of the Born–Mayer potential with the same ionic radii and repulsive parameters very similar to those used in the present paper[12, 13].

The partial contractions C_{ijklmn} and $C_{ijklmnn}$ of the T.O.E. and F.O.E. constants of CsCl, CsBr and CsI have been used above in conjunction with the second order elastic constants and the lattice constants to determine the ionic radii and the repulsive parameters for the cesium chloride-type cesium halides. In Table 11 the experimental[11, 39] and theoretical data are compared. Fair agreement for the T.O.E. and F.O.E. constants is found, but as for the rocksalt-type alkali halides, the agreement for the second order elastic constants is less satisfactory. A really consistent and comprehensive theory of the elastic constants of second and higher order is thus still lacking and would require first principle calculations of the cohesive contributions and a better approximation for evaluating the mode average in the thermal effects.

5. SUMMARY AND CONCLUSIONS

The primary purpose of the present paper is to present the lattice sums for the Coulomb, van der Waals and repulsive contributions to the higher order elastic constants up to sixth order for the rocksalt and for the cesium chloride structures. In addition, numerical values are given for a few selected alkali halides of both structure types and are based on the Huggins–Mayer form of the Born–Mayer potential with ionic radii and repulsive parameters from Tosi and Fumi[17, 18] for the rocksalt-type alkali halides, and on a new set of ionic radii and repulsive parameters determined from the available second, third and fourth order elastic constants for the cesium-type alkali halides. Thermal effects are only roughly taken into account by calculating the data for the room temperature lattice constants. Improved calculations should simultaneously consider better numerical values for the repulsive parameters, many body effects, deviations from the Born–Mayer form of the short range repulsive interactions and a better calculation of thermal effects.

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Table 11. Comparison of experimental and theoretical second order elastic constants $c_{\mu\nu}$ and partial contractions $\gamma^{(3)}_{\mu\nu}$ and $\gamma^{(4)}_{\mu\nu}$ of third and fourth order elastic constants (10^{12} dyn/cm^2), respectively, at 300°K

		c_{11}	c_{12}	c_{44}	$\gamma^{(3)}_{11}$	$\gamma^{(3)}_{12}$	$\gamma^{(3)}_{44}$	$\gamma^{(4)}_{11}$	$\gamma^{(4)}_{12}$	$\gamma^{(4)}_{44}$
CsCl	Exp.	0.367	0.088	0.081	-4.42	-2.17	-2.45	70.0	40.0	44.1
	Theor.	0.506	0.066	0.066	-5.81	-2.34	-2.34	82.4	40.2	40.2
CsBr	Exp.	0.306	0.081	0.075	-3.64	-1.91	-2.15	58.1	34.1	40.6
	Theor.	0.425	0.064	0.064	-5.02	-2.21	-2.21	73.5	38.9	38.9
CsI	Exp.	0.245	0.067	0.063	-3.01	-1.55	-1.79	48.1	27.4	34.3
	Theor.	0.337	0.055	0.055	-4.27	-1.94	-1.94	66.6	35.6	35.6

Experimental data are from Refs. [11, 39] and were used in the least squares fit for the determination of the repulsive parameters. $c_{\mu\nu}$ are adiabatic quantities, $\gamma^{(3)}_{\mu\nu}$ and $\gamma^{(4)}_{\mu\nu}$ intermediate adiabatic–isothermal values.

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APPENDIX 1

Cauchy relations

For convenience, all Cauchy relations for the second through sixth order elastic constants are listed here (in Voigt notation):

$$c_{12} = c_{44} \tag{A1.1}$$

$$c_{112} = c_{166} \tag{A1.2a}$$

$$c_{123} = c_{144} = c_{456} \tag{A1.2b}$$

$$c_{1112} = c_{1166} \tag{A1.3a}$$

$$c_{1122} = c_{1266} = c_{4444} \tag{A1.3b}$$

$$c_{1123} = c_{1144} = c_{1266} = c_{1456} = c_{4466} \tag{A1.3c}$$

$$c_{11112} = c_{11166} \tag{A1.4a}$$

$$c_{11122} = c_{11266} = c_{16666} \tag{A1.4b}$$

$$c_{11123} = c_{11144} = c_{11255} = c_{15566} = c_{11456} \tag{A1.4c}$$

$$c_{11223} = c_{11244} = c_{12366} = c_{12456} = c_{14444} = c_{44456} = c_{14466} \tag{A1.4d}$$

$$c_{111112} = c_{111166} \tag{A1.5a}$$

$$c_{111122} = c_{116666} = c_{111266} \tag{A1.5b}$$

$$c_{111222} = c_{112266} = c_{126666} = c_{6666666} \tag{A1.5c}$$

$$c_{111123} = c_{111456} = c_{111144} = c_{115566} = c_{111255} \tag{A1.5d}$$

$$c_{111223} = c_{112456} = c_{112366} = c_{111244} = c_{136666} = c_{125566} = c_{556666} = c_{166456} = c_{112255} = c_{114466} \tag{A1.5e}$$

$$c_{112233} = c_{123456} = c_{112344} = c_{114444} = c_{124455} = c_{144456} = c_{445566}. \tag{A1.5f}$$

The Cauchy relations for the elastic constants up to fourth order have been given before [2, 4, 16, 24].

APPENDIX 2

Calculation of the Coulomb sums

By forming the partial contractions of the Coulomb sums defined in eqn (2.7) with respect to the last index pair and using the Pythagorean theorem for the components of the interatomic distance vector $\bar{R}^{\mu\nu}_{mn}$ one obtains for cubic symmetry the following relations between Coulomb sums of successive order (in Voigt notation):

$$e_1 = e_{11} + 2e_{12} \tag{A2.1}$$

$$e_{11} = e_{111} + 2e_{112} \tag{A2.2a}$$

$$e_{12} = 2e_{112} + e_{123} \tag{A2.2b}$$

$$e_{111} = e_{1111} + 2e_{1112} \tag{A2.3a}$$

$$e_{112} = e_{1112} + e_{1122} + e_{1123} \tag{A2.3b}$$

$$e_{123} = 3e_{1123} \tag{A2.3c}$$

$$e_{1111} = e_{11111} + 2e_{11112} \tag{A2.4a}$$

$$e_{1112} = e_{11112} + e_{11122} + e_{11123} \tag{A2.4b}$$

$$e_{1122} = 2e_{11122} + e_{11223} \tag{A2.4c}$$

$$e_{1123} = e_{11123} + 2e_{11223} \tag{A2.4d}$$

$$e_{11111} = e_{111111} + 2e_{111112} \tag{A2.5a}$$

$$e_{11112} = e_{111112} + e_{111122} + e_{111123} \tag{A2.5b}$$

$$e_{11122} = e_{111122} + e_{111222} + e_{111223} \tag{A2.5c}$$

$$e_{11123} = e_{111123} + 2e_{111223} \tag{A2.5d}$$

$$e_{11223} = e_{112233} + 2e_{111223}. \tag{A2.5e}$$

The relations (A2.1) and (A2.2) have been given by Bross [19]. In eqn (A2.1) e_1 is equal to the Madelung number [19]. If e_1, e_{11}, e_{111}, e_{1111} and e_{11111} are known, eqns (A2.1)–(A2.4) allow the calculation of the remaining Coulomb sums $e_{12}; e_{112}; e_{123}; \ldots; e_{11112}, \ldots e_{11223}$ of second through fifth order. Since eqns (A2.5a)–(A2.5e) provide only 5 equations for the 7 sixth order Coulomb sums, two of these, say e_{111111} and e_{112233}, must be calculated independently.

According to Bross [19] the Coulomb sums with equal indices can be obtained by diffeentiation of the lattice sum

$$S(\alpha) = -\sum_{m,\mu} \frac{(-1)^n r}{[(X_1^{\frac{\mu}{m}})^2 + (X_2^{\frac{\mu}{m}})^2 + \alpha(X_3^{\frac{\mu}{m}})^2]} \tag{A2.6}$$

$$e_{\underbrace{11\ldots1}_{n}} = 3\frac{2^{2n}n!}{2n!}(-1)^n\left(\frac{\partial^n S(\alpha)}{\partial\alpha^n}\right)_{\alpha=1}. \tag{A2.7}$$

Here the summation over ν in eqn (2.7) is already carried out, because both $\nu = 1$ and $\nu = 2$ give the same contributions. By means of Madelung's method the lattice sum (A2.6) can be expressed as follows[19]:

$$S(\alpha) = \frac{2}{\sqrt{\alpha}}\left\{\ln 2 + 2\sum_{\substack{r=0\\ m\neq 0}}^{\infty}\cos\left[(2r+1)\pi\frac{z}{r}\right]K_0\left[(2r+1)\pi\frac{P_m}{r\sqrt{\alpha}}\right]\right\}. \tag{A2.8}$$

Here K_0 is the modified Hankel function of zeroth order, z is the distance to the nearest anion from the plane perpendicular to the chain of ions considered which passes through a cation at the coordinate origin, and P_m is the distance of the mth chain of ions from the straight line through the origin.

After performing the differentiation according to (A2.7) one obtains

$$e_1 = \sigma^{(0)} \tag{A2.9a}$$

$$e_{11} = 3\sigma^{(0)} - 4\sigma^{(1)} + \sigma^{(2)} \tag{A2.9b}$$

$$e_{111} = \frac{1}{5}[15\sigma^{(0)} - 23\sigma^{(1)} + 11\sigma^{(2)} - \sigma^{(3)}] \tag{A2.9c}$$

$$e_{1111} = \frac{1}{35}[105\sigma^{(0)} - 176\sigma^{(1)} + 122\sigma^{(2)} - 20\sigma^{(3)} + \sigma^{(4)}] \tag{A2.9d}$$

$$e_{11111} = \frac{1}{315}[945\sigma^{(0)} - 1689\sigma^{(1)} + 1518\sigma^{(2)} - 342\sigma^{(3)} + 33\sigma^{(4)} - \sigma^{(5)}] \tag{A2.9e}$$

$$e_{111111} = \frac{1}{3{,}465}[10{,}395\sigma^{(0)} - 19{,}524\sigma^{(1)} + 21{,}423\sigma^{(2)} - 5{,}946\sigma^{(3)} + 837\sigma^{(4)} - 48\sigma^{(5)} + \sigma^{(6)}] \tag{A2.9f}$$

with[19]

$$\sigma^{(2n)} = 4\sum_{r=0}^{\infty}\sum_{m}\cos\left[(2r+1)\pi\frac{z}{r}\right] \times\left[(2r+1)\frac{P_m}{r}\right]^{2n}K_0\left[(2r+1)\pi\frac{P_m}{r}\right] + 2\,\delta_{n,0}\ln 2 \tag{A2.10a}$$

$$\sigma^{(2n+1)} = 4\sum_{r=0}^{\infty}\sum_{m}\cos\left[(2r+1)\pi\frac{z}{r}\right] \times\left[(2r+1)\frac{P_m}{r}\right]^{2n}K_1\left[(2r+1)\pi\frac{P_m}{r}\right]. \tag{A2.10b}$$

The relations (A2.9a)–(A2.9c) have been given by Bross[19]. These relations were used for independently calculating the Coulomb sums for the rocksalt structure up to sixth order, except e_{112233}, for which no expression can be obtained from Madelung's method.

ERRATUM

R. C. HOLLINGER and G. R. BARSCH: Higher Order Elastic Constants of Alkali Halides. J. Phys. Chem Solids 37, 845-855 (1976).

A decimal error has occurred for the value of the van der Waals lattice sum h^U_{123} in Table 2. The correct value is 0.0122 (and not 0.1221). Consequently, the dipole-dipole van der Waals contribution to the T.O.E. constant c_{123} for NaCl in Table 7 is 0.006×10^{12} dyn/cm^2 (and not 0.03×10^{12} dyn/cm^2). Furthermore, the total calculated values of c_{123} reported in Tables 7, 8 and 9 have to be corrected as follows:

	c_{123} (in 10^{12} dyn/cm^2)	
	Reported	Corrected
LiF	1.00	0.97
LiCl	0.38	0.37
NaF	0.62	0.55
NaCl	0.28	0.25
KF	0.39	0.32
KCl	0.21	0.17
RbCl	0.19	0.14

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