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Analysis of the elastic properties of alkali halides

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A quantitative explanation for the breakdown of the Cauchy relation for elastic constants of alkali halides has been presented in terms of overlap integrals for neighbor ions using the Lowdin-Lundqvist formulation of the many-body potential. Values of the Cauchy deviation (c_{12}-c_{44}) are found to present close agreement with experimental data. The analysis has been extended to evaluate the third-order elastic constants and the pressure derivatives of the second-order elastic constants of NaCl-structure alkali halides. An adequate model for the interionic potentials has been developed by considering the short-range repulsive interactions between first and second nearest neighbors and van der Waals dipole-dipole interactions. The results obtained in the present paper compare well with recent experimental data.

I. INTRODUCTION

One of the most striking features exhibited by typical ionic crystals, viz., alkali halides, is that these crystals do not satisfy the Cauchy relation ($c_{12}=c_{44}$) for elastic constants at any temperature.[1,2] The earlier attempts to explain the Cauchy breakdown have been reviewed by Dick.[3] Three mechanisms have been proposed to account for the failure of the Cauchy relation in alkali halides. The first mechanism considers the role of the anharmonic effects.[4,5] The second mechanism takes account of the fact that in a strained cubic crystal, ions are no longer at points of cubic symmetry and find themselves in inhomogeneous electric fields. These induce quadrupole moments on the ions which interact electrostatically with the ion monopoles and with one another in a non-single-body manner. This leads to an expected deviation from the Cauchy relation, the magnitude of which has been estimated by Herpin.[6] The third mechanism, which takes into account the many-body forces arising from the nonorthogonality of the Heitler-London crystal wave functions, has been adopted by Lowdin[7] and Lundqvist.[8] The fact that even the low-temperature data on elastic constants do not satisfy the Cauchy relation reveals the importance of other mechanisms in addition to concerning first of all anharmonic effects. The second mechanism adopted by Herpin[5] yields always a positive value for $c_{12}-c_{44}$, whereas the experimental data indicate that $c_{12}-c_{44}$ is negative for many alkali halides. Thus it becomes obvious that the consideration of the third mechanism concerning many-body forces is essential to explain the breakdown of the Cauchy relation.

Lowdin's quantum-mechanical treatment, although far more fundamental, is much more complicated and needs great computational labor. This treatment has been extended by several investigators[9] to study the binding energies of ionic crystals composed of small ions, e.g., LiF, NaF. It was emphasized by Lundqvist,[8] by analyzing the formulation of Lowdin, that only the three-body forces make a significant contribution to the many-body potential in ionic solids. Lundqvist introduced a charge-transfer parameter f to develop a formulation for investigating the effect of the three-body potential on the cohesive and elastic properties of ionic solids. The parameter f can be determined from fundamental considerations using the values of the overlap integrals. In the absence of these integrals Lundqvist suggested an alternative method for determining the charge-transfer parameter from elastic constants. Verma, Singh, and their co-workers[10-15] have recently followed Lundqvist's approach to study the lattice-dynamical, dielectric, elastic, and photoelastic behavior of ionic crystals. However, the charge-transfer parameter determined phenomenologically by previous investigators[10-15] leads to inconsistent values of crystal binding energies.[16] In fact, such a determination is based on a forced condition according to which the breakdown of the Cauchy relation is entirely due to the existence of a three-body potential. This may not be strictly valid.

In the present paper we derive the charge-transfer parameter from the values of the overlap integrals[17] for nearest-neighbor ions and using the Lundqvist original formula. It is found that such a determination leads to the correct sign of the Cauchy discrepancy in almost all the alkali halides. After describing the Cauchy discrepancy in terms of Lundqvist's three-body forces, we have formulated the interionic potentials in alkali halides following the recent scheme of Catlow *et al.*[18] According to this scheme, the van der Waals dipole-dipole interaction is also considered along with second-neighbor overlap repulsive interactions.

The paper is organized as follows. In Sec. II we propose a method for calculating the Cauchy discrepancy $c_{12}-c_{44}$ on the basis of Lundqvist's formula. The relevant expressions for the third-order elastic (TOE) constants and the pressure derivatives of the second-order elastic (SOE) constants are given in Sec. III. The method of calculation and interionic potential forms are also described in Sec. III. The results are discussed and compared with experimental data in Sec. IV. The conclusions are summarized in Sec. V.

II. BREAKDOWN OF THE CAUCHY RELATION

As already emphasized in the Introduction, the consideration of a many-body or three-body potential is essential to explain the breakdown of the Cauchy relation. Lundqvist[8] investigated the effect of the three-body potential and derived the following expressions for the SOE constants of NaCl-structure crystals[12,13]:

$$c_{11}=\frac{e^2}{4a^4}\left[-5.112\epsilon(\epsilon+12f)+A_1+\frac{A_2+B_2}{2}+9.3204\epsilon\left(a\frac{df}{da}\right)\right], \tag{1}$$

$$c_{12}=\frac{e^2}{4a^4}\left[1.391\epsilon(\epsilon+12f)+\frac{A_2-B_2}{4}+9.3204\epsilon\left(a\frac{df}{da}\right)\right], \tag{2}$$

$$c_{44}=\frac{e^2}{4a^4}\left(2.556\epsilon(\epsilon+12f)+B_1+\frac{A_2+3B_2}{4}\right). \tag{3}$$

where e is the electron charge, a is the nearest-neighbor distance in equilibrium, A and B are the short-range force constants, and f is the three-body charge-transfer parameter introduced by Lundqvist. ϵ is the valence of the ion. Lundqvist obtained a formula for f by considering an infinite plane orthogonal to the line joining the nearest neighbors to divide the overlap region. He, however, does not specify the coordinates of this plane. The most appropriate choice of how to divide the overlap region between neighboring ions is that adopted by Dick and Overhauser[19] which is based on the consideration of ionic radii. The exchange charge is situated, on the line joining the two ions, at a distance r_+ from the center of the positive ion and r_- from the center of the negative ion.[19] According to this description we can rewrite the Lundqvist formula as follows:

$$f=\left(\frac{r_- - r_+}{a}\right)\sum_{ij}S_{ij}^2, \tag{4}$$

where S_{ij} is the overlap integral $\int U_i(1)U_j(1)d\tau_1$. The ionic radii are defined such that

$$r_+ + r_- = a. \tag{5}$$

Equations (4) and (5) yield

$$f=\left(1-\frac{2r_+}{a}\right)\sum_{ij}S_{ij}^2. \tag{6}$$

It is clear from Eq. (6) that f takes its largest value when the positive ion is very small and tends gradually to zero and becomes negative when the positive ion increases in size (Table I). This prediction is in complete accordance with the previous

TABLE I. Values of input data.

Crystal	a (Å)[a]	r_+ (Å)[b]	r_- (Å)[b]	f_0	c_{11} (10^{11} dynes/cm^2)
LiF	1.996	0.60	1.36	3.313	12.46[a]
LiCl	2.539	0.60	1.81	5.788	6.074[a]
LiBr	2.713	0.60	1.95	6.941	4.721[a]
LiI	2.951	0.60	2.16	7.600	2.540[c]
NaF	2.295	0.95	1.36	3.798	10.85[a]
NaCl	2.789	0.95	1.81	9.133	5.733[a]
NaBr	2.954	0.95	1.95	11.44	4.800[a]
NaI	3.194	0.95	2.16	12.80	3.761[a]
KF	2.648	1.33	1.36	−0.2386	7.570[a]
KCl	3.116	1.33	1.81	12.54	4.832[a]
KBr	3.262	1.33	1.95	17.82	4.17[a]
KI	3.489	1.33	2.16	24.68	3.38[a]
RbF	2.789	1.48	1.36	−4.067	6.527[a]
RbCl	3.259	1.48	1.81	10.65	4.297[a]
RbBr	3.410	1.48	1.95	17.23	3.863[a]
RbI	3.628	1.48	2.16	25.97	3.210[a]

[a] Reference 18.
[b] Reference 20.
[c] Reference 13(b).

result.[8] Following the work of Hafemeister and Flygare[17] we can write

$$\sum S_{ij}^2 = A_{ij}\exp(-r/\rho_{ij})\,, \tag{7}$$

where A_{ij} and ρ_{ij} are constants for nearest-neighbor overlaps. From Eqs. (6) and (7) we obtain

$$f = f_0 \exp(-r/\rho_{ij})\,, \tag{8}$$

where

$$f_0 = A_{ij}\left(1 - \frac{2r_+}{a}\right). \tag{9}$$

It should be mentioned that an equation similar to (8) was suggested by Cochran[21] and used by Singh and Shanker[22] on empirical grounds without making any investigation of the nature of f_0.

The Cauchy deviation obtained from Eqs. (2) and (3) is

$$c_{12} - c_{44} = \frac{e^2}{4a^4}\left[9.3204a\left(\frac{df}{dr}\right)_{r=a}\right], \tag{10}$$

where df/dr can be obtained from Eqs. (8) and (9) as follows:

$$\left(\frac{df}{dr}\right)_{r=a} = -\frac{f_0}{\rho_{ij}}\exp(-a/\rho_{ij})\,. \tag{11}$$

With the help of Eqs. (10) and (11) it is possible to make a quantitative estimation of $c_{12} - c_{44}$. The calculated values of $c_{12} - c_{44}$ for 16 alkali halides are given in Table II. Input data on c_{11}, the equilibrium distance a, the ionic radii r_+ and r_-, and the values of f_0 calculated from Eq. (9), using A_{ij} from Hafemeister and Flygare,[17] are given in Table I. For the sake of comparison we have also included in Table II the experimental values of $c_{12} - c_{44}$.

TABLE II. Values of the Cauchy discrepancy (10^{11} dynes/cm^2).

	$c_{12} - c_{44}$ (10^{11} dynes/cm^2)		
	Calculated		Experimental
Crystal	Present study	a	b
LiF	−0.84	0.326	−2.12
LiCl	−0.33	0.309	−0.39
LiBr	−0.25	0.269	−0.24
LiI	−0.18	0.212	−0.10
NaF	−0.27	−0.813	−0.68
NaCl	−0.20	0.154	−0.14
NaBr	−0.17	0.225	−0.11
NaI	−0.13	0.253	0.06
KF	0.01	−1.18	0.01
KCl	−0.15	−0.233	−0.09
KBr	−0.15	−0.118	−0.10
KI	−0.15	−0.014	−0.06
RbF	0.11	−1.18	0.24
RbCl	−0.10	−0.321	0.01
RbBr	−0.12	−0.193	−0.02
RbI	−0.13	−0.077	−0.02

[a] Reference 3.
[b] Reference 2.

III. EVALUATION OF THE TOE CONSTANTS AND THE PRESSURE DERIVATIVES OF THE SOE CONSTANTS

Using Born's theory of homogeneous deformation one can obtain the relevant expressions for the TOE constants and the pressure derivatives of the SOE constants of NaCl-type crystals[13,23] as follows:

$$c_{111} = \frac{e^2}{4a^4}\left[37.556\epsilon(\epsilon + 12f) + C_1 - 3A_1 + \frac{C_2 - 3A_2 - 9B_2}{4} + 13.980\epsilon\left(a^2\frac{d^2f}{da^2}\right) - 89.305\epsilon\left(a\frac{df}{da}\right)\right], \tag{12}$$

$$c_{112} = \frac{e^2}{4a^4}\left[-4.836\epsilon(\epsilon + 12f) + \frac{C_2 - 3A_2 + 3B_2}{8} + 4.660\epsilon\left(a^2\frac{d^2f}{da^2}\right) - 18.640\epsilon\left(a\frac{df}{da}\right)\right], \tag{13}$$

$$c_{166} = \frac{e^2}{4a^4}\left[-7.166\epsilon(\epsilon + 12f) - 2(B_1 + B_2) + \frac{C_2 - 3A_2 + 3B_2}{8} + 5.564\epsilon\left(a\frac{df}{da}\right)\right], \tag{14}$$

$$c_{123} = \frac{e^2}{4a^4}\left[2.717\epsilon(\epsilon + 12f) + 16.692\epsilon\left(a\frac{df}{da}\right)\right], \tag{15}$$

$$c_{144} = \frac{e^2}{4a^4}\left[2.717\epsilon(\epsilon + 12f) + 5.564\epsilon\left(a\frac{df}{da}\right)\right], \tag{16}$$

$$c_{456} = \frac{e^2}{4a^4}[2.717\epsilon(\epsilon + 12f)]\,, \tag{17}$$

$$\frac{dc_{44}}{dp} = -\Omega^{-1}\left[-11.389\epsilon(\epsilon + 12f) + A_1 - 3B_1 + \frac{C_2 + 2A_2 - 10B_2}{4} + 44.652\epsilon\left(a\frac{df}{da}\right)\right], \tag{18}$$

$$\frac{dK}{dp} = -(3\Omega)^{-1}\left[13.975\epsilon(\epsilon + 12f) + C_1 - 3A_1 + C_2 - 3A_2 - 167.764\epsilon\left(a\frac{df}{da}\right) + 41.94\epsilon\left(a^2\frac{d^2f}{da^2}\right)\right], \tag{19}$$

and

$$\frac{dS}{dp} = -(2\Omega)^{-1}\left[23.676\epsilon(\epsilon+12f)+C_1+\frac{C_2+6A_2-6B_2}{4}-51.0748\epsilon\left(a\frac{df}{da}\right)+13.98\epsilon\left(a^2\frac{d^2f}{da^2}\right)\right], \tag{20}$$

where

$$\Omega = -2.330\epsilon(\epsilon+12f)+A_1+A_2 + 27.961\epsilon\left(a\frac{df}{da}\right).$$

The short-range potential parameters are defined as follows:

$$A_1 = 8a^3\left(\frac{\partial^2 v_1(r)}{\partial r^2}\right)_{r=a}, \tag{21a}$$

$$B_1 = 8a^2\left(\frac{\partial v_1(r)}{\partial r}\right)_{r=a}, \tag{21b}$$

$$C_1 = 8a^4\left(\frac{\partial^3 v_1(r)}{\partial r^3}\right)_{r=a}, \tag{21c}$$

$$A_2 = 16a^3\left(\frac{\partial^2 v_2(r)}{\partial r^2}\right)_{r=\sqrt{2}a}, \tag{22a}$$

$$B_2 = 8\sqrt{2}\,a^2\left(\frac{\partial v_2(r)}{\partial r}\right)_{r=\sqrt{2}a}, \tag{22b}$$

$$C_2 = 16\sqrt{2}\,a^4\left(\frac{\partial^3 v_2(r)}{\partial r^3}\right)_{r=\sqrt{2}a}. \tag{22c}$$

The short-range potentials between nearest neighbors and next nearest neighbors are expressed in the following forms:

$$v_1'(r) = \frac{b}{e^2}\beta_{+-}\exp(r_+ + r_- - r)/\rho \tag{23}$$

and

$$v_2'(r) = \frac{b}{e^2}\left[\beta_{++}\exp(2r_+/\rho)+\beta_{--}\exp(2r_-/\rho)\right] \times \exp(-r/\rho) - \frac{C}{e^2 r^6}, \tag{24}$$

where the β_{ij} are the Pauling's coefficients, b and ρ are the repulsive parameters. C is the van der Waals dipole-dipole coefficient. $v_1'(r)$ and $v_2'(r)$ are related to the Lundqvist potential as follows:

$$v_1(r) = v_1'(r) + \frac{\epsilon\alpha_M}{a}f, \tag{25}$$

$$v_2(r) = v_2'(r), \tag{26}$$

where α_M is the Madelung constant. The potential parameters b and C are calculated from the crystal equilibrium condition and the expression for c_{11} [Eq. (1)] which yield

$$b = \frac{\frac{e^2\rho}{8a}\left(\frac{4c_{11}a^3}{e^2}+\frac{1.617(1+12f)}{a}+32.621f'-8\alpha_M af''\right)}{\left(\frac{a}{\rho}-3\right)\beta_{+-}\exp(r_+ + r_- - a)/\rho+\left(\frac{a}{\rho}-\frac{7}{\sqrt{2}}\right)\left[\beta_{++}\exp\left(\frac{2r_+}{\rho}\right)+\beta_{--}\exp\left(\frac{2r_-}{\rho}\right)\right]\exp\left(\frac{-\sqrt{2}a}{\rho}\right)}, \tag{27}$$

$$C = \frac{4}{3}\frac{ba^7}{\rho}\left\{\beta_{+-}\exp(r_+ + r_- - a)/\rho+\sqrt{2}\left[\beta_{++}\exp\left(\frac{2r_+}{\rho}\right)+\beta_{--}\exp\left(\frac{2r_-}{\rho}\right)\right]\exp\left(\frac{-\sqrt{2}a}{\rho}\right)\right\} - \frac{e^2a^6}{6}\left(8\alpha_M f'+\frac{1.165}{a}(1+12f)\right). \tag{28}$$

In the above expressions we have put $\epsilon = 1$ for alkali halides. f' and f'' are given as follows:

$$f' = \left(\frac{df}{dr}\right)_{r=a} = -\frac{f_0}{\rho_{ij}}\exp(-a/\rho_{ij}), \tag{29}$$

$$f'' = \left(\frac{d^2f}{dr^2}\right)_{r=a} = \frac{f_0}{\rho_{ij}^2}\exp(-a/\rho_{ij}). \tag{30}$$

Values of b and C calculated from Eqs. (27) and (28) are given in Table III. We have calculated the TOE constants and the pressure derivatives of the SOE constants for 16 NaCl-structure crystals. In Table IV we give the calculated values of the short-range force constants A_1, B_1, C_1, A_2, B_2, and C_2. The calculated values of the TOE constants are reported in Table V and pressure derivatives of the SOE constants in Table VI.

IV. RESULTS AND DISCUSSIONS

In the present calculations of the TOE constants and pressure derivatives of the SOE constants we have used the charge-transfer parameter f derived from Eq. (8). As values of the repulsive hardness parameter ρ we used those derived from the overlap integrals.[24] It should be mentioned that previous workers[12,13,25] determined ρ from the data fitting of elastic constants. They used the input data on elastic constants and the lattice parameter corresponding to room temperature. This

TABLE III. Calculated values of b and C.

Crystal	b (10^{-12} erg)	C (10^{-60} erg cm^6) Present study	Previous workers a	Previous workers b
LiF	0.173	26	36	18
LiCl	0.138	220	271	113
LiBr	0.130	357	490	183
LiI	0.091	326	1036	363
NaF	0.178	25	115	46
NaCl	0.162	199	492	180
NaBr	0.165	392	786	271
NaI	0.164	800	1465	482
KF	0.136	112	370	167
KCl	0.157	372	1150	452
KBr	0.158	511	1663	605
KI	0.162	918	2724	924
RbF	0.113	196	556	278
RbCl	0.148	521	1589	691
RbBr	0.159	790	2237	898
RbI	0.164	1354	3537	1330

[a] Reference 34.
[b] Reference 35.

is, however, unjustified because their expressions for the elastic constants are valid only at 0 K and thermal effects contribute significantly to the breakdown of the Cauchy relation. Moreover, these investigators[12,13,25] do not simultaneously consider the contributions arising from the second-neighbor repulsive interactions and van der Waals interactions. The effect of these inconsistencies is that the values of ρ calculated in previous work[12,13] are strongly deviating from the corresponding values based on recent experimental data.[26] On the other hand, the values of ρ based on overlap integrals[24] and used in the present study are close to the experimental values.[26] In our calculations we have used low-temperature (helium temperature) data on the lattice parameter and elastic constants recently compiled by Catlow *et al.*[18] The use of low-temperature data removes the ambiguities arising from the anharmonic effect.

The most remarkable feature of the present analysis is the evaluation of the charge-transfer parameter from the overlap integrals and thereby the successful prediction of the Cauchy breakdown in alkali halides. In the past there have been several attempts[3,27] to explain the Cauchy breakdown but none of these has been quantitatively successful. Recently Bartels ans Son[27] tried to correlate the Cauchy breakdown and ionicity of the chemical bond.[28] These investigators concluded that there is no direct relationship between the two quantities. Their conclusion is independent of the ionicity model considered and is valid even at low temperatures. A more detailed investigation of the Cauchy breakdown in alkali halides has been made by Dick[3] on the basis of the exchange-charge model proposed by Dick and Overhauser.[19] This model is not very successful in predicting the observed $c_{12}-c_{44}$. Values of $c_{12}-c_{44}$ calculated by Dick are included in Table II for the sake of comparison. From these we observe that the exchange-charge interaction model of Dick gives the wrong sign of $c_{12}-c_{44}$ in eight alkali halides. On the other hand, the method based on the Lundqvist formulation using the nearest-neighbor overlap integrals adopted in the present study predicts not only the correct sign for the Cauchy deviation but also its magnitude in close agreement with experimental values.

It is evident from the calculated values of the

TABLE IV. Calculated values of the short-range force constants.

Crystal	A_1	B_1	C_1	A_2	B_2	C_2
LiF	6.30	−0.764	−51.4	5.84	−0.452	−68.9
LiCl	5.05	−0.559	−45.1	10.4	−0.655	−139
LiBr	4.55	−0.506	−40.6	11.6	−0.704	−156
LiI	2.77	−0.282	−25.7	13.2	−0.928	−172
NaF	9.80	−1.10	−86.8	1.63	−0.088	−23.1
NaCl	9.28	−0.982	−87.2	4.67	−0.222	−70.7
NaBr	9.08	−0.965	−85.1	5.77	−0.241	−89.9
NaI	8.48	−0.886	−80.8	7.98	−0.321	−126
KF	11.7	−1.30	−105	−0.476	0.138	−1.37
KCl	13.4	−1.37	−130	−0.026	0.159	−12.1
KBr	13.5	−1.35	−134	0.641	0.127	−22.7
KI	13.5	−1.32	−137	1.87	0.090	−44.0
RbF	12.1	−1.35	−109	−0.951	0.211	1.95
RbCl	14.2	−1.45	−139	−1.02	0.253	−0.451
RbBr	15.0	−1.50	−149	−0.969	0.288	−4.41
RbI	15.4	−1.50	−156	−0.153	0.267	−19.0

TABLE V. Calculated values of TOE constants (10^{12} dynes/cm^2). Experimental values are given within parentheses.

Crystal	c_{111}	c_{112}	c_{166}	c_{123}	c_{144}	c_{456}
LiF	−17.1	−5.37	−5.86	0.881	0.981	1.03
LiCl	−7.94	−3.50	−3.70	0.334	0.373	0.393
LiBr	−6.00	−2.95	−3.11	0.256	0.286	0.301
LiI	−3.10	−2.32	−2.43	0.183	0.204	0.215
NaF	−17.0	−1.61	−1.78	0.529	0.561	0.578
	(−14.8)[a]	(−2.7)[a]	(−1.14)[a]	(2.8)[a]	(0.46)[a]	
NaCl	−8.81	−1.37	−1.50	0.232	0.256	0.268
	(−8.8)[a]	(−0.571)[a]	(−0.611)[a]	(0.284)[a]	(0.258)[a]	(0.271)[a]
NaBr	−7.19	−1.30	−1.14	0.183	0.203	0.213
NaI	−5.49	−1.25	−1.33	0.133	0.148	0.156
KF	−12.8	−0.565	−0.560	0.320	0.319	0.319
KCl	−7.92	−0.305	−0.404	0.146	0.164	0.172
	(−7.01)[a]	(−0.244)[a]	(−0.245)[a]	(0.133)[a]	(0.127)[a]	(0.118)[a]
KBr	−6.85	−0.316	−0.422	0.117	0.136	0.145
KI	−5.50	−0.345	−0.449	0.085	0.103	0.112
RbF	−10.5	−0.455	−0.381	0.275	0.261	0.254
RbCl	−7.10	−0.172	−0.239	0.125	0.137	0.143
	(−6.71)[b]	(−0.180)[b]	(−0.17)[b]	(0.11)[b]	(0.11)[b]	(0.14)[b]
RbBr	−6.39	−0.145	−0.226	0.100	0.114	0.121
RbI	−5.31	−0.163	−0.252	0.073	0.088	0.096

[a] Reference 13(b).

[b] Reference 39.

TOE constants listed in Table V that c_{123}, c_{144}, and c_{456} are positive and c_{111}, c_{112}, and c_{166} are negative for all the alkali halides under study. The magnitudes of the TOE constants decrease continuously as one goes from the fluoride to the corresponding iodide of the same alkali metal. A similar decrement occurs also if one goes from the lithium to the rubidium salt in the same halide series. The experimental values of the TOE constants are known only for NaCl, KCl, RbCl, and NaF. On the other hand, the pressure derivatives of the SOE constants have been measured for all

TABLE VI. Values of pressure derivatives of SOE constants.

	dc_{44}/dp		dS/dp		dK/dp	
Crystal	Calculated	Experimental[a]	Calculated	Experimental[a]	Calculated	Experimental
LiF	1.95	1.38	1.71	3.60	4.84	5.30[b]
LiCl	2.77	1.70	1.40	3.79	5.50	5.63[b]
LiBr	2.94	1.80	1.25	3.75	5.59	5.68[b]
LiI	3.38	1.96	0.74	4.00	5.68	6.15[b]
NaF	0.452	0.205	3.67	4.79	4.74	5.25[c]
NaCl	1.41	0.37	3.18	4.79	5.31	5.38[c]
NaBr	1.69	0.46	2.98	4.83	5.46	5.44[c]
NaI	2.14	0.61	2.67	4.80	5.72	5.58[c]
KF	−0.375	−0.43	4.65	5.25	4.74	5.38[c]
KCl	−0.106	−0.39	5.12	5.61	5.04	5.46[c]
KBr	0.146	−0.33	5.00	5.68	5.18	5.47[c]
KI	0.574	−0.24	5.00	6.03	5.40	5.56[c]
RbF	−0.982	−0.70	4.80	4.93	4.79	5.69[d]
RbCl	−0.457	−0.56	5.05	5.88	5.01	5.62[d]
RbBr	−0.371	−0.55	5.68	6.03	5.12	5.59[d]
RbI	−0.038	−0.51	5.59	6.26	5.30	5.60[d]

[a] Experimental values are those cited in Ref. 13(b).

[b] Reference 40.

[c] Reference 41.

[d] Reference 42.

the alkali halides under investigation. We observe from Tables V and VI that our calculated values are in reasonably good agreement with experimental data. It should be mentioned here that the measurements of Bensch[29] for the TOE constants of NaF seem to be doubtful. It is evident from the experimental values of the TOE constants for NaCl, KCl, and RbCl that the Cauchy discrepancies among the TOE constants are not very large and are of about the same order as those among the SOE constants, viz., $c_{12}-c_{44}$. This result, according to our theoretical analysis, should hold true for all the alkali halides. However, the experimental values of the TOE constants for NaF show substantially large discrepancies which vary roughly from about 15% to more than 500%. Such large discrepancies in NaF, which has a small Cauchy discrepancy among the SOE constants, are not expected. There is thus a definite ground for a revision of the measurements on this crystal.

A few comments concerning the previous theoretical studies on TOE constants and the pressure derivatives of the SOE constants of alkali halides are here in order. The values of the TOE constants calculated by Nranyan[30] show very large deviations (more than 100%) from the experimental ones. Ghate[31] has remarked that Nranyan's values of the electrostatic contributions to the TOE constants were in error. Ghate rectified this error and calculated the values of the TOE constants using the Born model.[32] However, the Born model considers only the central pairwise interactions and is therefore not capable of explaining the Cauchy breakdown properly. Moreover, the results obtained by Ghate do not agree satisfactorily with experimental data.

Puri and Verma[12] considered the effect of three-body interactions but short-range repulsion was limited to nearest neighbors only. This resulted in rather poor agreement with experiment. In subsequent studies[13] these workers considered the second-neighbor interactions arising from the repulsion but neglected the contribution arising from the van der Waals interactions. The fact that the van der Waals interactions contribute significantly to the crystal binding of ionic solids has been established by recent quantum-mechanical[33] as well as phenomenological studies[18,34]. It is pertinent to mention here that Tripathi and Goyal[25] considered the second-neighbor interactions arising solely from the van der Waals interactions estimated by Mayer.[35] Their method of calculation is not applicable and does not yield good results even for all the NaCl-structure alkali halides. The cause of this discrepancy is that Tripathi and Goyal did not consider the second-neighbor repulsive interactions. Also the van der Waals potentials derived by Mayer and used by Tripathi and Goyal are somewhat underestimated. The foregoing discussion thus reveals that in an adequate theory of the elastic constants of ionic crystals, one should consider the short-range repulsion up to second neighbors as well as the van der Waals interactions.[22]

It should be emphasised that in the present study there are only two parameters, viz., the repulsive strength parameter b and the van der Waals dipole-dipole interaction coefficient C. These have been determined from the crystal equilibrium condition and the elastic constant c_{11}. The values of the dipole-dipole coefficient C calculated in the present study are compared in Table III with those obtained by other investigators from theoretical methods based on the London-Margenau[36] and the Slater-Kirkwood[37] formulas. In the previous work[12,13,25] there were at least five parameters, viz., b, ρ, f, df/dr, and d^2f/dr^2. The first four parameters were derived from the crystal equilibrium condition and the SOE constants (c_{11}, c_{12}, and c_{44}). The last parameter d^2f/dr^2 was derived from one of the TOE constants or from one of the pressure derivatives of the SOE constants. In view of such a calculation of d^2f/dr^2, the agreement obtained by previous investigators[12,13,25] is rather forced. In the present work we have determined f, df/dr, and d^2f/dr^2 from the Lundqvist formula using overlap integrals and thereby reducing the number of parameters. The agreement between theory and experiment we obtained, without using any TOE constants or pressure derivatives of the SOE constants as input data, is particularly encouraging.

It is pertinent to stress here that the parametric values of f, df/dr, and d^2f/dr^2 obtained by previous workers[12,13,25] are not consistent with Eq. (8) and hence are unrealistic. The validity of this statement can be demonstrated by calculating the crystal energies of alkali halides under study. By considering the effect of the three-body potential, the crystal energy can be written as follows:

$$W = \alpha_M \frac{e^2}{r}\epsilon(\epsilon + 12f) + [M v_1'(r) + M' v_2'(r)]e^2 , \qquad (31)$$

where $\alpha_M = -1.747\,56$ and $M = M' = 12$.

We have calculated the crystal potential energy of 16 alkali halides using the parameters reported by Garg *et al.*[13] as well as those obtained in the present paper. These are compared in Table VII with experimental values based on thermodynamic data.[38] We note from Table VII that the crystal energies calculated from the parameters reported by Garg *et al.* are much lower than the experimental values. On the contrary, our calculated values of crystal energies are in close agreement with

TABLE VII. Cohesive energies (kcal/mole).

Crystal	Calculated a	 b	Experimental c
LiF	−225.9	−259.2	−246.7
LiCl	−117.2	−209.1	−203.2
LiBr	−94.9	−196.4	−194.2
LiI	−61.6	−181.1	−180.3
NaF	−194.7	−225.5	−219.5
NaCl	−136.0	−188.6	−187.1
NaBr	−115.7	−178.9	−178.5
NaI	−91.7	−167.1	−167.0
KF	−134.8	−195.7	−194.3
KCl	−120.8	−168.1	−170.2
KBr	−180.7	−161.2	−163.2
KI	−92.7	−151.7	−153.6
RbF	−112.0	−186.0	−185.8
RbCl	−106.1	−160.7	−163.6
RbBr	−99.3	−154.1	−157.2
RbI	−86.2	−145.7	−148.5

[a] Calculated using the potential parameters of Garg *et al.* [Ref. 13(b)].

[b] Calculated in the present study using our own potential parameters.

[c] Reference 38.

experiment for all the alkali halides. This demonstrates the adequacy of the approach adopted in the present paper.

V. SUMMARY AND CONCLUSIONS

We have thus studied the elastic behavior of alkali-halide crystals on the basis of the Lundqvist three-body potential. The notable contribution of the present study is the evaluation of the three-body charge-transfer parameter f from the values of the overlap integrals for nearest-neighbor ions. Such a determination of the charge-transfer parameter leads to a quantitative explanation of the Cauchy deviation in the crystals under study. It should be emphasized that no previous attempt has been successful in accounting for the observed $c_{12} - c_{44}$ quantitatively.

The values of f, df/dr, d^2f/dr^2 calculated in the present paper from Lundqvist's formula using overlap integrals are found to be more appropriate than those obtained previously[12,13,25] from the parametric approach. The parametric values of f, df/dr, and d^2f/dr^2 are not consistent with the crystal binding energies. On the other hand, the values obtained in the present study are capable of explaining the binding energy as well as the TOE constants and pressure derivatives of the SOE constants.

To summarize, the present study reveals the importance of the three-body interactions, the next-nearest-neighbor interactions, and the van der Waals interactions operative in alkali-halide crystals. The consideration of these interactions is essential to explain the cohesive and elastic properties of ionic solids.

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