Hellmann potential extended to next-nearest neighbors for alkali halide crystals

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The short-range Hellmann potential function exhibiting the characteristics of both the Born-Lande and the Born-Mayer potential functions has been extended to include the contributions of next-nearest neighbors and van der Waals interactions. It is further employed to calculate the isothermal bulk modulus (B_T) and its first- and second-order pressure derivatives (dB_T/dP, d^2B_T/dP^2), coefficient of volume expansion (β), adiabatic and isothermal Anderson Gruneisen parameters (δ_S and δ_T), and transverse- and longitudinal-optic-mode Gruneisen parameters (γ_{TO} and γ_{LO}) for NaCl-structure alkali halides. Computations have also been extended to calculate the Gruneisen parameter (γ) and mode Gruneisen parameter (q) using Slater, Dugdale and McDonald, and free-volume theories. The results are found to be in good agreement with experimental data.

I. INTRODUCTION

Recently several workers[1-3] have performed first-principles *ab initio* calculations for potentials in ionic crystals. These calculations are based on the theory of Gordon and Kim[4] for determining pair potentials for closed-shell systems from the charge densities of the free ions constituting the crystal. The method of Gordon and Kim is essentially based on the Thomas-Fermi-Dirac electron-gas model which has been criticized by Eggenhoffner, Murthi, and Gumi,[5] pointing out the lack of any self-consistency of treatment between electron density and potential. Due to the simplifying approximations and the parameter-free nature of the first-principles calculations, the results are generally less accurate than those derived from the parametrized models of the solids. These model potentials play a useful role in interpreting experimental results.

A number of short-range potential functions[6-10] have been proposed from time to time by different investigators, but none of them is capable of explaining all observed macroscopic properties of ionic crystals. The search for the potential function capable of explaining all the macroscopic properties of the crystals, therefore, still continues. The essential requirements of an ideal potential are as follows.

(i) It should be short range in nature, i.e., must fall sharply with increasing distances.

(ii) It should provide infinite repulsion at zero separation to avoid the mutual collapse of the ions into one another.

The Born-Lande (BL) inverse power form, initially proposed to explain the cohesive energy of crystals, satisfies both conditions cited above, but the results obtained by using this form are not very satisfactory. The Born-Mayer (BM) exponential form discussed very often in the literature does not satisfy the second requirement cited above, although it has a quantum-mechanical support behind it.

Hellmann[11] empirically proposed the repulsive potential function of the type

$$\phi(r)=\frac{b}{r}\exp(-r/\rho)\ , \tag{1}$$

which evidently satisfies the second condition and simultaneously has the advantage of both the BL and BM potential forms. A comparison of the rate of fall of the potential with distance is given in Table I for the sake of ready reference showing that the rate of fall is very steep in the case of the Hellmann potential. The Rydberg potential which provides for an attractive term seems to be the most unreliable potential, for the net interaction turns out to be attractive for larger distances, which is against the preliminary assumption. Moreover, it is not infinite even at $r=0$. The rate of fall of the Born-Mayer potential is nearly equal to that of the Hellmann potential but it also does not satisfy condition (ii) stated earlier. The Born-Lande potential, though, satisfies condition (i) but the fall is very slow. Similar is the case with the Narayan-Ramaseshan (NR) potential which neither becomes infinite at $r=0$ nor is the fall much steeper. Evidently the Hellmann potential seems to be the ideal in nature and needs further investigation.

Preliminary studies of the Hellmann potential conducted by many investigators[7,12,13] did not yield very encouraging results, because none of them tried to extend the potential up to second neighbors. It is well known that the second-neighbor contributions are quite significant (contributing 30–40 % to the cohesive energies of the alkali-halide crystals) and should not be ignored. Moreover, the van der Waals interactions contributing 10–15 % to cohesive energy of the ionic crystals, too, cannot be neglected.

We have in the present study not only extended the Hellmann potential up to second neighbors, but also have taken into account the van der Waals dipole-dipole and dipole-quadrupole interactions to calculate the isothermal bulk modulus and its first- and second-order pressure derivatives, the transverse- and longitudinal-optic mode Gruneisen parameters (γ_{TO} and γ_{LO}), the

TABLE I. Comparative study of Rydberg, Born-Mayer, Narayan-Ramaseshan, Born-Lande, and Hellmann potentials for NaCl crystal (taken as an example) showing the superiority of the Hellmann potential over the rest of the potentials.

Name of the potential	Form of the potential	Relative values of potential at $r=0$	$r=a$	$r=a\sqrt{2}$	$r=2a$
Rydberg[a]	$\lambda\exp(-br)$ $-\mu r\exp(-br)$	2366	1	−0.097	−0.0109
Born-Mayer[b] ($\rho=0.321$)	$B\exp(-r/\rho)$	6536	1	0.0263	1.8×10^{-4}
Narayan-Ramaseshan[c]	$A_+\exp(-r_+/\rho_+)$ $+A_-\exp(-r_-/\rho_-)$	62 000	1	0.0318	0.0035
Born-Lande ($n=9$)	A/r^n	∞	1	0.4453	1.97×10^{-7}
Hellmann ($\rho=0.358$)	$\frac{b}{r}\exp(-r/\rho)$	∞	1	0.0272	1.9×10^{-4}

[a]Reference 34.
[b]Reference 6.
[c]Reference 35.

Gruneisen parameter (γ), the mode Gruneisen parameter (q), and the Anderson Gruneisen parameters (δ_S and δ_T). It is worth noting that the results are very close to the experimental data. The mathematical analysis is presented in Sec. II while the results are discussed in Sec. III of the present paper. For the sake of comparison, the calculated values of different quantities using the Narayan and Ramaseshan[10] (NR) potential and the Rydberg[9] potential are also given in the respective tables.

II. MATHEMATICAL ANALYSIS

The lattice energy per ion pair of a diatomic crystal can be written as

$$\psi(r)=-\frac{\alpha_M(Ze)^2}{r}+\phi(r)-\frac{C}{r^6}-\frac{D}{r^8}\ , \tag{2}$$

where r is the equilibrium distance at zero external pressure. The first term of the right-hand side of Eq. (2) being the long-range electrostatic Madelung energy, C and D are the van der Waals dipole-dipole and dipole-quadrupole coefficients. The parameters b and ρ appearing in Eq. (1) have been evaluated by using the cohesive energy E, and the equilibrium condition

$$\frac{d\psi\gamma(A\gamma)}{dr}=0\ . \tag{3}$$

The potential expressed by Eq. (1) can be extended further to include the second-neighbor contribution as under

$$\phi(r)=n_1\left[\frac{b}{r}\exp\left[\frac{r_++r_--r}{\rho_{+-}}\right]\right]+\frac{n_2}{2}\left[\frac{b}{r'}\exp\left[\frac{2r_+-r'}{\rho_{++}}\right]+\frac{b}{r'}\exp\left[\frac{2r_--r'}{\rho_{--}}\right]\right]\ . \tag{4}$$

Here n_1 and n_2 are the number of nearest- and next-nearest neighbors and r' is the next-nearest-neighbor distance. In this equation, we have used different values of the softness parameter ρ_{ij} for different ion pairs given by

$$\rho_{ij}=\tfrac{1}{2}(\rho_{ii}+\rho_{jj}) \tag{5}$$

within the framework of the Smith distorsion model.[14] We have calculated the values of ρ_{ii} and ρ_{jj} employing the least-squares-fitting approximation and using the values of ρ_{ij} determined by the procedure discussed earlier, i.e., through Eq. (3).

From the definition of the bulk modulus, we have

$$B_T=-VP'\ . \tag{6}$$

Differentiating Eq. (6) we get

$$\frac{dB_T}{dP}=-1-V\frac{P''}{P'}\ . \tag{7}$$

Subsequent differentiation of this equation yields

$$\frac{d^2B_T}{dP^2}=-\frac{P''}{(P')^2}-\frac{VP'''}{(P')^2}+\frac{V(P'')^2}{(P')^3}\ , \tag{8}$$

where $P=-d\psi(r)/dV$ and P', P'', and P''' represent the first-, second-, and third-order derivatives of P with respect to volume at constant temperature.

The Gruneisen parameter γ ($=\beta VB_T/C_\gamma$), describing the thermodynamic behavior of the crystals, was evaluated by Slater[15] from the theory of elasticity. His expression for the vibrational velocities are valid only if the solid is under zero external pressure. Dugdale and McDonald[16] derived a more general expression for γ by including the effect of pressure. But these theories do not take into account the variation of Poisson's ratio with volume.[17] Vaschenko and Zubarov[18] developed a formulation for γ using the free-volume theory. Recently Migault and Romain[19] proposed a unification of these theories, taking into account the variation of Poisson's ratio with volume and evaluated a general expression for γ, giving

$$\gamma=-\frac{4-3s}{6}-\frac{V}{2}\frac{d^2(PV^s)/dV^2}{d(PV^s)/dV}\ , \tag{9}$$

where P is the pressure at volume V at absolute zero of temperature and s is a parameter which takes for all solids the value zero in Slater's theory, $\frac{2}{3}$ in the Dugdale and McDonald (DM) theory, and $\frac{4}{3}$ in the free-volume (FV) theory.

The mode Gruneisen parameter q at zero external pressure can be expressed as $q=d\ln\gamma/d\ln V$,

$$q=\frac{1}{2\gamma}\left\{s(1+s)-\frac{(1-s)VP''}{P'}-V^2\left[\frac{P'''}{P'}-\left[\frac{P''}{P'}\right]^2\right]\right\}. \tag{10}$$

The two Anderson (adiabatic and isothermal) parameters (δ_S and δ_T) related to pressure-independent temperature derivatives of adiabatic (B_s) and isothermal (B_T) bulk moduli can be written as

$$\delta_S=-\frac{1}{\beta}\left[\frac{\partial\ln B_S}{dT}\right]_P, \tag{11}$$

$$\delta_T=-\frac{1}{\beta}\left[\frac{\partial\ln B_T}{dT}\right]_P, \tag{12}$$

where β is the volume-expansion coefficient, given by

$$\beta=-\tfrac{3}{2}C_V\frac{[r^3\psi'''(r)-2r\psi'(r)]}{[r^2\psi''(r)-2r\psi'(r)]^2}. \tag{13}$$

Shanker and Singh[20] expressed the Anderson parameters with the help of thermodynamic equations in terms of volume-dependent and volume-independent contributions of adiabatic and isothermal bulk moduli (B_S and B_T) as follows:

$$\delta_S=-\left[\frac{\partial\ln B_S}{\partial\ln V}\right]_T-\frac{1}{\beta}\left[\frac{\partial\ln B_S}{\partial T}\right]_V, \tag{14}$$

$$\delta_T=-\left[\frac{\partial\ln B_T}{\partial\ln V}\right]_T-\frac{1}{\beta}\left[\frac{\partial\ln B_T}{\partial T}\right]_V. \tag{15}$$

A plausible assumption can be made to calculate temperature-independent volume dependence of the bulk modulus

$$\left[\frac{\partial\ln B_S}{\partial\ln V}\right]_T\simeq\left[\frac{\partial\ln B_T}{\partial\ln V}\right]_T, \tag{16}$$

which can be expressed in terms of interionic potential energy as follows:

$$\left[\frac{\partial\ln B_T}{\partial\ln V}\right]_T=\frac{1}{3}\left[\frac{r^3\psi'''(r)-3r^2\psi''(r)+4r\psi'(r)}{r^2\psi''(r)-2r\psi'(r)}\right]. \tag{17}$$

Values of δ_S and δ_T are calculated using Eqs. (14)–(17). Values of the first part on the right-hand side of Eqs. (14) and (15) are calculated from the Hellmann potential and the second part, related to the temperature derivatives of the bulk modulus at constant volume, are determined from thermoelastic data.[21,22] The coefficient of volume expansion (β) is calculated from Eq. (13).

Following Born and Huang, the force constant A can be expressed as

$$A=\tfrac{1}{3}\left[\phi_R''(r)+\frac{2}{r}\phi_R'(r)\right]=3krB_T, \tag{18}$$

where

$$\phi_R(r)=\phi(r)-\frac{C}{r^6}-\frac{D}{r^8} \tag{19}$$

represents short-range potential and $\phi_R'(r)$ and $\phi_R''(r)$ represent the first- and second-order derivatives of A with respect to r. Differentiation of the well-known Szigeti[23] relation

$$\left[\frac{\epsilon_0+2}{\epsilon_\infty+2}\right]\bar{\mu}\omega_{\rm TO}^2=A \tag{20}$$

with respect to V yields for the transverse-optic-mode Gruneisen parameter

$$\begin{aligned}\gamma_{\rm TO}&=-\frac{V}{\omega_{\rm TO}}\frac{d\omega_{\rm TO}}{dV},\\ \gamma_{\rm TO}&=\frac{1}{2}\left[\frac{1}{\epsilon_0+2}\left[\frac{Vd\epsilon_0}{dV}\right]-\frac{1}{\epsilon_\infty+2}\left[\frac{Vd\epsilon_\infty}{dV}\right]-\frac{V}{A}\frac{dA}{dV}\right].\end{aligned} \tag{21}$$

The longitudinal-optic-mode Gruneisen parameter $\gamma_{\rm LO}$ is related to $\gamma_{\rm TO}$ by the relation

$$\gamma_{\rm LO}=\gamma_{\rm TO}-\frac{1}{2}\left[\frac{V}{\epsilon_0}\frac{d\epsilon_0}{dV}-\frac{V}{\epsilon_\infty}\frac{d\epsilon_\infty}{dV}\right], \tag{22}$$

where ϵ_0 and ϵ_∞ are the static and electronic dielectric constants, respectively. $\bar{\mu}$ is the reduced mass of the ion pair and $\omega_{\rm TO}$ represents infrared-absorption frequency in the transverse-optic mode.

We have taken the experimental data on ϵ_0 and ϵ_∞ from Lowndes and Martin[24] and those on $Vd\epsilon_\infty/dV$ from Bendow *et al.*[25] and Mahmud, Kamath, and Scaife.[26] The experimental data on $Vd\epsilon_0/dV$ have been taken from Fontanella, Andeen, and Scheule[27] and Lowndes and Martin.[24]

III. RESULTS AND DISCUSSIONS

The results of computations carried out in the present work are reported in Tables II–VII. Table II contains the values of the model parameters calculated using Eqs. (1)–(3). Table III records the results on the isothermal bulk modulus and its first- and second-order pressure derivatives calculated in the present work along with their experimental values. A careful examination of Table III exhibits remarkable agreement for the isothermal bulk modulus (B_T), first- and second-order pressure derivatives of the isothermal bulk modulus (dB_T/dP and d^2B_T/dP^2) with experimental values. We have taken the values of ionic radii r_{ij} from Sysio.[28] The values of cohesive energy E have been taken from Ladd.[29] The values of van der Waals coefficients C and D are taken from the recent work of Shanker and Rajoria[30] for the

TABLE II. Calculated values of the repulsive strength parameter (b) and softness parameter ρ_+ and ρ_- for anions and cations, respectively, appearing in the Hellmann potential.

Crystal	b (10^{-20} ergs m/g mol)	ρ_+ (Å)	ρ_- (Å)
LiF	0.880	0.065	0.269
LiCl	0.865	0.065	0.281
LiBr	0.873	0.065	0.296
LiI	0.997	0.065	0.326
NaF	0.784	0.077	0.269
NaCl	0.867	0.077	0.281
NaBr	0.987	0.077	0.296
NaI	1.037	0.077	0.326
KF	1.276	0.114	0.269
KCl	1.138	0.114	0.281
KBr	1.144	0.114	0.296
KI	1.169	0.114	0.326
RbF	1.288	0.130	0.269
RbCl	1.222	0.130	0.281
RbBr	1.233	0.130	0.296
RbI	1.246	0.130	0.326

reasons discussed at length in Shanker and Agrawal.[31] Table IV shows the calculated values of the Gruneisen parameter γ using Slater,[15] Dugdale and McDonald,[16] and free volume[17] theories along with their experimental data. In Tables III–VII we have also recorded the results from our previous papers calculated using the Narayan-Ramaseshan[10] (NR) and Rydberg[9] potential for the sake of comparison. NR considers the ions as a compressible sphere assuming the short-range repulsive interaction of the type

$$\phi(r)=\phi_+ +\phi_- = A_+ \exp\left[-\frac{r_+}{\rho_+}\right] + A_- \exp(-r_-/\rho_-) \ . \tag{23}$$

The Rydberg potential

$$\phi(r)=\lambda \exp(-r/\rho)-\mu r \exp(-r/\rho) \ , \tag{24}$$

contrary to the traditional potential forms, assumes an attractive term providing for the mutual attraction between the nucleus of one ion with the electrons of the other ion. An analysis of the Tables III–VII shows the superiority of the Hellmann potential over other potentials. It is easy to see from the tables that the Slater's theory for γ and q could safely be discarded as it gives comparatively poor agreement with the experimental while the results using Dugdale and McDonald (DM) theories are in better agreement with the experiment. The simplified form of Eq. (9) gives a direct relationship between γ and dB_T/dP as under

$$\gamma=\frac{1}{6}+\frac{1}{2}\frac{dB_T}{dP}-\frac{s}{2} \ , \tag{25}$$

which further yields the following expressions:

$$\gamma_{\text{Slater}}=-\frac{1}{6}+\frac{1}{2}\frac{dB_T}{dP} \ , \tag{26}$$

TABLE III. Calculated values of the isothermal bulk modulus (B_T) and its first- (dB_T/dP) and second- (d^2B_T/dP^2) order pressure derivatives using the NR, Rydberg, and Hellmann potential along with their experimental data.

	B_T (10^{10} N m^{-2})				dB_T/dP				$(-d^2B_T/dP^2)10^{-11}$ Pa^{-1}			
Crystal	Calc.[a]	Calc.[b]	Calc.[c]	Expt.[d]	Calc.[c]	Calc.[b]	Calc.[e]	Expt.[f]	Calc.[a]	Calc.[b]	Calc.[e]	Expt.[g]
LiF	0.299	0.653	0.682	0.674	4.79	3.84	4.58	5.30	27.1	7.4	12.5	
LiCl	0.306	0.323	0.342	0.301	4.79	4.61	4.76	5.63	19.9	10.6	20.5	
LiBr	0.279	0.278	0.247	0.238	4.79	4.78	4.94	5.68	21.1	19.8	31.4	
LiI	0.263	0.214	0.205	0.178	4.69	4.95	4.86	6.15	19.7	24.8	35.1	
NaF	0.171	0.436	0.461	0.471	4.88	3.94	4.69	5.30	49.5	10.7	14.9	
NaCl	0.181	0.275	0.260	0.240	4.80	4.66	4.97	5.63	36.2	17.3	28.0	
NaBr	0.158	0.216	0.227	0.197	4.88	4.53	5.10	5.68	42.7	25.0	31.2	
NaI	0.162	0.173	0.169	0.151	4.71	4.75	5.10	6.15	35.4	32.7	46.9	49±14
KF	0.124	0.316	0.319	0.306	5.18	4.00	5.21	5.38	70.8	12.6	21.2	
KCl	0.134	0.172	0.188	0.176	4.94	4.82	5.20	5.46	45.0	44.9	40.6	
KBr	0.121	0.153	0.164	0.148	5.08	4.55	5.27	5.47	58.0	37.0	52.5	
KI	0.117	0.123	0.126	0.117	4.98	4.69	5.31	5.56	55.0	47.6	71.6	53±15
RbF	0.104	0.247	0.288	0.270	6.21	4.37	5.44	5.69	136.1	21.1	24.7	
RbCl	0.139	0.161	0.167	0.158	5.88	4.63	5.32	5.62	90.2	36.0	52.1	58±21
RbBr	0.137	0.137	0.152	0.134	5.31	4.69	5.11	5.59	51.6	43.5	68.2	75±25
RbI	0.118	0.110	0.113	0.106	5.26	4.74	5.33	5.60	60.7	54.9	77.0	77±17

[a]NR potential (Ref. 37).
[b]Rydberg potential (Ref. 38).
[c]NR potential (Ref. 36).
[d]Reference 39.
[e]Present study.
[f]References 21 and 22.
[g]References 40 and 41.

TABLE IV. Calculated values of the Gruneisen parameter (γ) using Slater, Dugdale and McDonald (DM), and free-volume (FV) theories along with experimental data.

	γ (Slater)			γ (DM)			γ (FV)			γ (expt.)		
Crystal	a	b	c	a	b	c	a	b	c	d	e	f
LiF	2.23	1.76	2.12	1.90	1.42	1.79	1.56	1.09	1.45	1.63		
LiCl	2.23	2.14	2.21	1.89	1.80	1.88	1.56	1.47	1.54	1.81		
LiBr	2.23	2.23	2.30	1.90	1.89	1.97	1.56	1.56	1.63	1.94	2.48	
LiI	2.18	2.31	2.24	1.85	1.97	1.91	1.51	1.64	1.58	2.19	2.38	
NaF	2.27	1.80	2.18	1.94	1.47	1.85	1.60	1.14	1.51	1.51	1.86	
NaCl	2.23	1.96	2.32	1.90	1.63	1.99	1.57	1.29	1.65	1.61	1.69	2.66
NaBr	2.27	2.10	2.38	1.94	1.77	2.05	1.61	1.43	1.72	1.64	1.75	2.74
NaI	2.19	2.21	2.38	1.86	1.87	2.05	1.52	1.54	1.72	1.71	1.72	2.78
KF	2.42	1.84	2.44	2.09	1.50	2.10	1.75	1.17	1.77	1.52	1.71	
KCl	2.30	2.24	2.43	1.97	1.91	2.10	1.64	1.56	1.77	1.49	1.59	2.52
KBr	2.37	2.11	2.67	2.04	1.77	2.14	1.71	1.44	1.80	1.50	1.69	2.50
KI	2.32	2.18	2.49	1.99	1.85	2.15	1.66	1.51	1.82	1.53	1.27	2.56
RbF	2.94	2.02	2.55	2.60	1.68	2.22	2.27	1.35	1.89	1.40	1.66	
RbCl	2.77	2.15	2.49	2.44	1.82	2.16	2.11	1.68	1.82	1.39	1.45	2.60
RbBr	2.49	2.18	2.39	2.16	1.84	2.05	1.82	1.51	1.72	1.42	1.37	2.65
RbI	2.51	2.20	2.48	2.18	1.87	2.15	1.85	1.54	1.82	1.56	1.32	2.61

[a]NR potential (Ref. 37).
[b]Rydberg potential (Ref. 38).
[c]Present study.
[d]Based on thermodynamic data (Ref. 39).
[e]Based on the lattice-dynamical theory (Ref. 42).
[f]Based on the finite-strain theory (Ref. 43).

TABLE V. Calculated values of the mode Gruneisen parameter (q) using Slater, Dugdale and McDonald (DM), and free-volume (FV) theories along with experimental data.

	q (Slater)			q (DM)			q (FV)			
Crystal	a	b	c	a	b	c	a	b	c	q (Expt.)[d]
LiF	1.82	1.38	2.00	1.41	0.86	1.65	1.12	0.69	1.43	0.98
LiCl	1.37	1.17	1.59	0.88	0.66	1.14	0.47	0.21	0.79	1.46
LiBr	1.32	1.37	1.68	0.82	0.89	1.30	0.40	0.48	0.90	1.61
LiI	1.19	1.37	1.60	0.58	0.81	1.16	0.24	0.37	0.81	1.48
NaF	1.87	1.30	1.57	1.46	0.85	1.13	1.20	0.53	0.78	1.08
NaCl	1.47	1.10	1.57	1.00	0.57	1.11	0.62	0.11	0.73	1.14
NaBr	1.49	1.23	1.48	1.02	0.80	1.00	0.63	0.39	0.60	1.46
NaI	1.31	1.28	1.66	0.82	0.78	1.21	0.40	0.36	0.85	1.44
KF	1.81	1.08	1.39	1.38	0.58	0.89	1.04	0.18	0.45	1.34
KCl	1.34	1.72	1.57	0.85	1.30	1.10	0.42	0.98	0.71	1.53
KBr	1.50	1.34	1.74	1.02	0.87	1.29	0.62	0.48	0.92	1.24
KI	1.39	1.34	1.82	0.90	0.86	1.38	0.48	0.45	1.02	0.99
KbF	2.42	1.30	1.39	2.02	0.82	0.89	2.11	0.44	0.44	1.80
RbCl	2.27	1.34	1.75	1.87	0.86	1.30	1.55	0.47	0.93	1.84
RbBr	1.42	1.37	1.53	1.09	0.89	1.06	0.48	0.49	0.66	1.69
RbI	1.43	1.37	1.76	0.93	0.89	1.29	0.49	0.49	0.93	1.59

[a]NR potential (Ref. 37).
[b]Rydberg potential (Ref. 38).
[c]Hellmann potential (present study).
[d]References 21 and 22.

TABLE VI. Calculated values of isothermal and adiabatic Anderson parameters (δ_T and δ_S) and the coefficient of volume expansion (β) along with their experimental data.

	δ_T				δ_S				β (10^{-4} k^{-1})			
Crystal	Calc.[a]	Calc.[b]	Calc.[c]	Expt.[d]	Calc.[a]	Calc.[b]	Calc.[c]	Expt.[e]	Calc.[a]	Calc.[f]	Calc.[c]	Expt.[g]
LiF	5.62	4.67	5.41	6.00	3.96	3.01	3.75	3.56	2.51	0.86	1.05	1.00
LiCl	6.21	6.03	6.98	6.77	3.37	3.19	3.34	4.09	1.33	1.05	1.18	1.32
LiBr	6.33	6.33	6.48	7.01	3.24	3.23	3.39	4.12	1.23	1.11	1.43	1.50
LiI	6.12	6.38	6.29	7.32	3.26	3.52	3.43	4.06	0.99	1.25	1.34	1.80
NaF	5.48	4.54	5.29	5.77	4.28	3.34	4.09	3.75	3.41	1.01	1.21	0.96
NaCl	5.40	5.26	5.57	5.85	4.20	4.06	4.37	3.80	1.34	1.17	1.32	1.19
NaBr	5.83	5.48	6.05	6.23	3.93	3.58	4.15	4.11	1.84	1.23	1.35	1.26
NaI	5.71	5.75	6.10	6.43	3.71	3.75	4.10	4.13	1.36	1.29	1.44	1.37
KF	5.12	4.94	6.15	6.20	4.24	3.06	4.27	4.08	3.43	0.97	1.34	1.02
KCl	5.87	5.75	6.12	6.22	4.01	3.89	4.27	4.38	1.89	1.33	1.44	1.11
KBr	5.62	5.09	5.81	5.88	4.54	4.01	4.73	4.02	1.90	1.22	1.48	1.16
KI	5.31	5.02	5.63	5.76	4.65	4.36	4.98	3.93	1.57	1.29	1.58	1.23
RbF	7.41	5.57	6.64	6.80	5.01	3.17	4.24	4.97	4.42	1.02	1.37	0.94
RbCl	7.17	5.92	6.61	6.76	4.59	3.34	4.03	4.93	1.79	1.19	1.63	1.03
RbBr	6.46	5.84	6.26	6.60	4.16	3.54	3.96	4.72	1.58	1.25	1.36	1.08
RbI	6.32	5.80	6.36	6.52	4.20	3.68	4.24	4.47	1.54	1.31	1.58	1.23

[a]NR potential (Ref. 37).
[b]Present study using the Rydberg potential.
[c]Present study using the Hellmann potential.
[d]Reference 20.
[e]Reference 30.
[f]Rydberg potential (Ref. 38).
[g]Reference 39.

TABLE VII. Calculated values of longitudinal- and transverse-optic-mode Gruneisen parameter (γ_{LO} and γ_{TO}) along with their experimental data.

	γ_{LO}				γ_{TO}			
Crystal	Calc.[a]	Calc.[b]	Calc.[c]	Expt.[d]	Calc.[e]	Calc.[b]	Calc.[c]	Expt.[d]
LiF	1.38	0.75	1.15	0.97	2.83	2.62	2.60	2.35±0.16
LiCl	1.26	1.27	1.61		2.88	2.66	3.23	
LiBr	1.20	1.76	1.27		3.26	3.37	3.33	
NaF	0.83	0.87	0.99	0.76	2.24	2.07	2.40	2.08±0.18
NaCl	1.42	2.12	1.29	0.97	2.75	2.53	2.62	2.35±0.16
NaBr	1.42	1.31	1.35	1.09	2.85	2.65	2.78	2.37±0.20
NaI	1.63	1.46	1.38		2.87	2.80	2.62	
KF	1.41	0.83	1.41		2.49	2.13	2.49	
KCl	1.48	1.08	1.41	1.19	2.64	2.23	2.57	2.28±0.18
KBr	1.62	1.12	1.44	0.97	2.68	2.25	2.50	2.06±0.13
KI	1.61	1.31	1.41	1.12	2.58	2.23	2.48	2.20±0.06
RbF	1.28	0.39	1.46		2.74	1.65	2.92	
RbCl	1.69	1.17	1.45	1.04	2.78	2.19	2.55	2.16±0.10
RbBr	1.71	1.23	1.35	1.33	2.79	2.24	2.43	2.39±0.16
RbI	1.79	1.32	1.48	1.15	2.77	2.15	2.46	2.09±0.15

[a]Calculated in the present work using the NR potential.
[b]Rydberg potential (Ref. 38).
[c]Present study using the Hellmann potential.
[d]Reference 44.
[e]NR potential (Ref. 37).

$$\gamma_{DM}=\gamma_{Slater}-\tfrac{1}{3}\ , \tag{27}$$

$$\gamma_{FV}=\gamma_{Slater}-\tfrac{2}{3}=\gamma_{DM}-\tfrac{1}{3}\ . \tag{28}$$

It is worth noting that the formula for γ is not satisfied even for the experimental data on dB_T/dP, the main reason for this being the diversity in the data on γ as observed from Table IV. Reverse calculations using the experimental values of dB_T/dP and γ yield the average value of s as 1.5 for Li halides, 1.85 for Na halides, 2.00 for K halides and 2.5 for Rb halides, i.e., no uniform value of s can be chosen to satisfy the formula for γ. The formula for γ therefore needs further investigation and refinement of the theory which will be the scope of future work. The values of the mode Gruneisen parameter (q) given in Table V, calculated from the DM theory using the Hellmann potential, are found to be close to 1 which is in agreement with the assumption $q\simeq 1$ initially made by Anderson[32] and Swenson.[33] The values of δ_S, δ_T, B, γ_{TO}, γ_{LO} calculated from the Hellmann potential are also in better agreement with experimental data than the other potential forms taken into consideration.

In the present work, we have neglected the many-body interactions for the sake of simplicity. Moreover, in this simplified version of the Hellmann potential we have taken the uniform value of b for all ion pairs (cation-cation, anion-anion, cation-anion). The Hellmann potential can further be improved to incorporate the correction factors along with other minor modifications. The application of the Hellmann potential to predict the elastic and photoelastic constants will be our next step of study.

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