An Exponential Function for Repulsive Interaction Energy Term
I. Application to Alkali Halides

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The appropriateness of a suitably modified Varshni-Shukla potential has been tested for a series of alkali halide crystals by determining the numerical values of the potential parameters involved, using Hildebrand's equation of state and thereby computing a few lattice properties. Comparison between the different sets of theoretical and experimental results infers that the present theoretical values exhibit an improvement over those of other workers, using a similar approach but with different potential energy functions. It is concluded that the modified V—S potential function is a good choice for explaining the behaviour of alkali halide lattices.

1. Introduction

On the basis of pair potential functions the macroscopic properties of diatomic crystals have already been computed by different workers[1–5]. The general approach is to assume an analytical form of the pair potential and then to exploit the well known equilibrium properties to evaluate the parameters of the potential function. Once the potential function is determined the lattice properties can be easily computed. In the present communication we have investigated the simple and basic properties viz. cohesive energy (W), infrared absorption frequency (ν_0), Grüneisen parameter (γ) and Anderson-Grüneisen parameter (δ) of the alkali halide crystals using the Varshni-Shukla potential (V – S)[6] in the modified form suggested by Patel et al.[7]. Though central forces can not exactly account for the behaviour of crystal lattices, by virtue of their simplicity such potentials are useful for various purposes. The suitability of such an approach in understanding the mechanical and thermal properties of alkali halide lattices seems to be demonstrated by the results of the present investigations.

2. Theory

The crystal energy may be expressed as the sum of the coulombic attractive energy, the overlap repulsive energy and the van der Waals attractive energy terms. Thus the potential energy of a crystal per pair of ions for the modified V-S potential can be expressed as

$$\psi(r) = -\frac{\alpha e^2}{r} + \lambda \exp(-b\, r^{3/2}) - \frac{C}{r^6} - \frac{D}{r^8} \qquad (1)$$

where $\psi(r)$ is the energy per cell, α the Madelung constant, e the electronic charge, r the interionic equilibrium separation distance, C and D the van der Waals constants and λ and b the potential parameters.

Equation (1) is associated with two approximations. First, the contributions of second and more remote neighbours to the repulsion energy have been neglected and secondly, no account has been taken for the deformation of ions due to the electrostatic crystal potential.

The contribution of second neighbours has been discussed by Born and Huang[8], who prefered to ignore it in favour of simple calculations. Later on Tosi[9] estimated its magnitude and found it to be negligible. The effect of third and more remote neighbours may be neglected owing to the short range character of the forces involved. The contribution to the lattice energy arising from the deformation of ions has been estimated by de Wette and it has been observed that for symmetrical crystals this contribution is very small[9].

(a) Evaluation of Potential Parameters

The potential parameters λ and b can be evaluated by employing the Hildebrand room temperature lattice conditions[10] at negligible pressure which can be expressed as

$$\left[\frac{\mathrm{d}\psi(r)}{\mathrm{d}r}\right]_{r=r_0} = \frac{3\, v\, T\, \alpha_v}{\beta\, r_0} \qquad (2)$$

and

$$\left[\frac{\mathrm{d}^2\psi(r)}{\mathrm{d}r^2}\right]_{r=r_0} = \frac{9\, v}{\beta\, r_0^{\,2}}\, F_{T,P} \qquad (3)$$

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where v is the volume of the unit cell, α_v the volume thermal expansion coefficient, r_0 the equilibrium interionic distance, β the compressibility, and $F_{T,P}$ a correction factor.

Equations (2) and (3) in conjunction with Eq. (1) yield,

$$\lambda = \frac{2K}{3} \frac{\exp(b\, r_0^{3/2})}{b\, r_0^{3/2}} \tag{4}$$

and

$$b = \frac{\frac{5}{6} \cdot \alpha e^2/r_0 + 15\, C/r_0^6 + 76\, D/3\, r_0^8 + 3\, v/\beta - vT\, \alpha_v 2\, \beta}{(K/2)\, r_0^{3/2}} \tag{5}$$

where

$$K = \left(\frac{\alpha e^2}{r_0} + \frac{6\, C}{r_0^6} + \frac{8\, D}{r_0^8} - \frac{3\, v\, T\, \alpha_v}{\beta} \right).$$

The parameters λ and b have been evaluated from Eqs. (4) and (5). The experimental input data which have been used to determine the parameters are reported in Table 1.

The data for the interatomic distance, r_0, and the compressibility, β, have been taken from Cubicciotti[3], for the thermal expansion, α_v, from Kumar[11] and for van der Waal constants, C and D, from Born and Huang[8]. Data for static and high frequency dielectric constants which are also reported in Table 1 have been taken from Kittel[12]: these constants are required below.

(b) Cohesive Energy

The cohesive energy per mole, W can be computed using the relation[8]

$$W = -[N\, \psi(r_0) + \varepsilon_0] \tag{6}$$

where N is the Avogadro number and ε_0 the zero point energy per mole.

Computed values of cohesive energy using Eq. (6) for the alkali halide series are reported in Table 2 along with the experimental[8, 13] as well as with other theoretical[14] values for the sake of comparison.

(c) Infrared Absorption Frequency

Following Born and Huang[8] and Krishnan and Roy[15], an expression for the force constant "f" may be expressed as,

$$f = \frac{1}{3} \left[\Phi''(r_0) + \frac{2}{r_0}\, \Phi'(r_0) \right] \tag{7}$$

where $\Phi'(r_0)$ and $\Phi''(r_0)$ are the first and second derivatives of the $\Phi(r)$, at $r = r_0$. $\Phi(r)$ includes

Table 1. Input Experimental Data.

Crystal	r_0 (10^{-8} cm) Ref. 3	β (10^{-12} cm^2/dyne) Ref. 3	α_v (10^{-6} deg^{-1}) Ref. 11	C (10^{-60}) Ref. 8	D (10^{-72}) Ref. 8	ε_0 Ref. 12	ε_∞ Ref. 12
LiF	2.014	1.43	34.0	18	11	8.90	1.90
LiCl	2.570	3.17	44.0	113	164	12.00	2.70
LiBr	2.751	3.90	50.0	183	190	13.12	3.20
LiI	3.000	5.30	59.0	366	470	11.02	2.38
NaF	2.317	2.06	36.0	46	31	5.10	1.70
NaCl	2.820	3.97	40.0	180	180	5.90	2.25
NaBr	2.989	4.75	43.0	271	300	6.40	2.60
NaI	3.237	6.21	48.3	482	630	6.60	2.91
KF	2.674	3.14	36.7	167	150	5.50	1.50
KCl	3.147	5.50	38.3	452	560	4.85	2.10
KBr	3.298	6.45	40.0	605	800	4.90	2.30
KI	3.533	8.07	45.0	924	1420	5.10	2.70
RbF	2.815	3.66	31.6	228	290	6.50	1.90
RbCl	3.291	6.16	36.0	691	960	4.90	2.20
RbBr	3.445	7.38	38.0	898	1340	4.90	2.30
RbI	3.671	9.00	43.0	1330	2240	5.00	3.60
CsF	3.004	4.25	31.6	495	600	—	—
CsCl	3.571	5.55	45.5	1530	2600	7.20	2.60
ClBr	3.720	6.28	46.3	2070	3600	6.50	2.80
CsI	3.956	7.83	48.6	2970	5800	5.65	3.00

Table 2. Values of Cohesive Energy W in K Cal/Mole.

Crystal	Exptl. Ref. 8	Theoret. Eq. (6)	Theoret. Ref. 3	Theoret. Ref. 14
LiF	246.0 *	242.6	238.9	245.4
LiCl	201.6	197.6	198.2	203.0
LiBr	191.5	186.2	186.1	191.9
LiI	180.6	172.8	175.3	178.1
NaF	218.0 *	217.5	218.8	218.2
NaCl	184.7	185.9	183.4	185.9
NaBr	175.9	175.5	174.4	177.0
NaI	166.3	163.9	162.2	165.9
KF	193.0 *	193.3	185.2	194.7
KCl	167.8	167.9	164.0	169.9
KBr	161.2	161.6	161.9	162.7
KI	152.8	150.9	149.0	153.4
RbF	—	186.0	172.7	186.4
RbCl	163.6	163.1	156.5	164.3
RbBr	158.0	156.3	151.2	157.6
RbI	149.7	149.0	143.4	149.1
CsF	—	183.1	164.2	179.2
CsCl	157.8	155.3	148.1	155.9
CsBr	152.3	149.2	144.9	151.1
CsI	145.4	143.3	137.4	193.6

* These values have been taken from Ref. 13.

all the interaction energy terms of Eq. (1) except the coulombic energy term ($-\alpha e^2/r$). The values of the force constant obtained from Eq. (7) have been reported in Table 3. Once the force constant f has been calculated from Eq. (7), the infrared absorption frequency may be computed by a simple and direct approach through the assumption of a central pairwise potential energy function coupled

Table 3. Values of force constants f and infrared absorption frequency ν_0.

Crystal	f (10^4) Eq. (7)	ν_0 (10^{12} cm sec^{-1}) Exptl. Ref. 19	Theoret. Eq. (8)	Theoret. Ref. 20	Theoret. Ref. 21	Theoret. Ref. 21
LiF	2.2603	9.12	8.36	5.22	15.78	15.87
LiCl	1.3530	6.12	6.13	4.04	11.19	10.89
LiBr	1.1921	5.13	5.55	3.79	10.23	7.09
LiI	9.9129	4.32	4.93	3.68	9.60	8.21
NaF	2.0099	7.38	6.95	3.87	9.78	9.78
NaCl	1.3943	4.92	5.08	3.22	5.46	6.81
NaBr	1.0927	4.05	4.01	2.66	5.73	5.46
NaI	9.8325	3.51	3.72	2.34	5.25	4.62
KF	1.3995	5.76	4.95	—	—	—
KCl	1.0463	4.32	4.02	2.51	4.50	5.25
KBr	9.9740	3.48	3.37	1.88	4.29	4.14
KI	8.3019	3.03	2.97	1.74	3.90	3.54
RbF	1.3919	4.80	4.44	—	—	—
RbCl	1.0519	3.57	3.50	2.20	4.50	4.23
RbBr	9.0582	2.70	2.56	1.62	4.17	3.09
RbI	7.3476	2.25	2.35	1.45	2.91	2.61
CsF	—	3.81	—	—	—	—
CsCl	9.6100	2.97	2.87	1.81	—	—
CsBr	8.5173	2.22	2.115	1.49	—	—
CsI	8.7023	—	2.05	—	—	—

with the consideration of electronic polarizability, which may be expressed by the equation,

$$\nu_0 = 2\,\pi^{-1}(f/m)^{1/2}\,(\varepsilon_\infty + 2)^{1/2}\,(\varepsilon_0 + 2)^{-1/2} \qquad (8)$$

where m is the reduced mass per ion pair and ε_0 and ε_∞ are the dielectric constants at static and high frequencies respectively. Though it is a highly suspect assumption to treat the electronic polarisation and the short range forces as independent, results obtained using this assumption [5, 16–18] encourage us to adopt Eq. (8) for the computation of ν_0. The values of ν_0 computed on the basis of expression (8) are reported in Table 3 together with observed [19] as well as theoretical [20, 21] values computed by other workers.

(d) Grüneisen Constant

On the basis of the expression for the internal energy given by Slater [22], recently Misra and Sharma [23] have derived an expression for the Grüneisen constant in terms of the derivatives of the potential energy function, which may be written as

$$\gamma = -\frac{r_0}{6}\,[\psi'''(r_0)]\,[\psi''(r_0)]^{-1} \qquad (9)$$

where $\psi''(r_0)$ and $\psi'''(r_0)$ refer to the second and third derivatives of $\psi(r)$ at $r = r_0$.

Equation (9) in conjunction with Eq. (1) yields

$$\gamma = \frac{r_0}{6}\left[\frac{\dfrac{6\,\alpha e^2}{r_0^{\,4}} + \dfrac{336C}{r_0^{\,9}} + \dfrac{720D}{r_0^{\,11}} + \dfrac{K}{2}\left(\dfrac{9\,b}{2\,r_0^{\,3/2}} + \dfrac{1}{2\,r_0^{\,3}} - 9\,b^2/2\right)}{\dfrac{2\,\alpha e^2}{r_0^{\,3}} + \dfrac{42\,C}{r_0^{\,8}} + \dfrac{72\,D}{r_0^{\,10}} + \dfrac{K}{2}\left(\dfrac{1}{r_0^{\,2}} - \dfrac{3\,b}{r_0^{\,1/2}}\right)}\right] \qquad (10)$$

where K is represented by the same expression as in the case of Eqs. (4) and (5).

The computed values of γ, obtained from Eq. (10) are reported in Table 4 along with the experimental [24] and other theoretical [24, 25] values.

(e) Anderson-Grüneisen Parameter

The Anderson-Grüneisen parameter was suggested by Anderson [26] during the interpretation of the emperical parameters associated with Watchman's [27] equation. In order to compute the Anderson-Grüneisen parameter directly from the model consideration, Sharma and Tripathi [28] successfully derived a general expression for δ, which can be expressed as

$$\delta = \frac{(1+\gamma)\,[f'(v_0) - v_0\,f''(v_0)] - v_0^{\,2}\,f'''(v_0) + 7\,P/3}{(1+\gamma)\,f'(v_0) + v_0\,f''(v_0) + P} \qquad (11)$$

where

$$P = \frac{\alpha\,e^2}{3\,v_0^{\,4/3}}\,(\gamma - 1/3)\,.$$

In Eq. (11), $f'(v_0)$, $f''(v_0)$ and $f'''(v_0)$ are the first, second and third derivatives of $f(v)$ at $v = v_0$; $f(v)$ refers to the potential function as a function of volume instead of interatomic separation and includes all interaction terms of Eq. (1) except the first i. e. the coulombic interaction.

Two more sets of δ values have been computed using the two relations given by Chang [29]

$$\delta = 2\,\gamma \qquad (12)$$

and

$$\delta = 2\,\gamma - 2/3\,. \qquad (13)$$

Values of the Anderson-Grüneisen Parameter calculated from Eqs. (11), (12) and (13) are presented in Table 5 along with the experimental data [30] and other equivalent theoretical [31] values for the sake of comparison.

Results and Discussion

In Table 2 there seems to be an excellent agreement between the present theoretical values of cohesive energy and the corresponding observed data for nearly all the alkali halides. The present values, calculated with the aid of the modified V-S potential exhibit a marked improvement over those obtained earlier using the Pauling model. In case of two crystals only (LiCl and LiI), the Pauling model results are superior to the present ones. The poor response of the Pauling model may be attributed to the neglect of the significant contribution of dipole-dipole and dipole-quadrupole interactions. The Born-Mayer model employed by Cubbiciotti [3] yielded good results, which are very close to the observed data but when compared to the present values it is found that in fifty percent of the cases (viz. KX, NaCl, NaBr, RbF, and RbCl) the modified V-S potential is a better approximation. However for the salts of lithium the present model does not seem to be a good choice as regards the evaluation of cohesive energy. The neglect of the deformation of the ions in the potential energy function might be responsible for this weakness.

The calculated values of reststrahlen frequencies given in Table 3 are quite close to the experimental ones. These values are invariably better than the corresponding values of Srivastava et al.[20]. Both values of Mitra and Joshi[21] (presented in last two columns) are very high for all the cases. It may be observed from Table 3 that the success of the present approach in predicting the infrared absorption behaviour of the alkali halides is remarkable, the credit for which partly goes to the consideration of polarization in Equation (8). Theoretically speaking the rigid ion approach does not allow to consider any polarisation effect except that involved in the van der Waals interactions, but the hybridized scheme where the polarisation effect has been introduced through the expression for absorption frequency instead of the model itself, converts the whole procedure into a simple and satisfactory one. It may be noted from the same Table that for the fluorides the results show the poorest agreement. This is true not only for the present results but also for all other reported theoretical results. Raman[32] has attributed this shift of behaviour of the fluorides to their high melting point indicating a tight binding and high compressibility. This shift may be observed also by considering the density of the alkali halide salts. It may be noted that the density, which is very high for the fluorides, drops to a very low value for the chlorides and then increases slowly for the bromides and iodides. In this light it may be suggested that for a better understanding of the nature of the interionic potential in fluorides, these may be treated separately.

A survey of Table 4, where various results for γ are presented, shows that the present results in general agree well with the experimental ones. The experimental results are not the directly observed ones but are calculated[24] by feeding the observed data for the volume thermal expression, the compressibility and the specific heat into an equation defining γ. A close examination of Table 4 suggests that the present results are a little higher than the experimental ones except for halides of lithium and a few fluoride crystals. The values for chloride and bromide for same metal are nearly equal. It may be observed that the values of γ are small for light crystals and large for heavier ones, showing its dependence upon the specific volume. Comparing

Table 4. Values of Grüneisen Parameter γ.

Crystal	Exptl. Ref. 24	Theoret. Eq. (10)	Theoret. Ref. 25	Theoret. * Ref. 24	Theoret. ** Ref. 24
LiF	1.75	1.04	1.80	1.79	2.20
LiCl	1.78	1.32	1.77	1.97	2.19
LiBr	2.02	1.42	1.66	2.02	2.16
LiI	2.22	1.49	1.69	2.09	2.30
NaF	1.72	1.51	1.63	1.99	2.20
NaCl	1.74	1.69	1.76	2.28	2.34
NaBr	1.81	1.68	1.80	2.21	2.41
NaI	1.90	1.78	1.87	2.27	2.48
KF	–	1.51	1.73	2.17	2.37
KCl	1.60	1.73	1.88	2.28	2.49
KBr	1.58	1.83	1.91	2.33	2.53
KI	1.72	1.87	1.97	2.40	2.60
RbF	–	1.67	1.81	2.24	2.44
RbCl	1.53	1.89	1.93	2.02	2.58
RbBr	1.50	1.92	1.95	2.26	2.58
RbI	1.73	1.99	2.01	2.25	2.66
CsF	–	1.43	–	–	–
CsCl	2.74	2.07	2.13	2.25	2.83
CsBr	1.93	2.02	–	–	–
CsI	2.00	2.37	–	–	–

* Using Born-Mayer potential and present approach.

** Using Born-model.

Table 5. Values of Anderson-Grüneisen Parameter δ.

Crystal	**Exptl. Ref. 30**	Exptl. Ref. 30	Theoret. Eq. (11)	Theoret. Eq. (12)	Theoret. Eq. (13)	Theoret. * Ref. 31	Theoret. ** Ref. 31
LiF	—	4.12	2.04	2.08	1.42	2.32	2.17
LiCl	—	4.63	2.32	2.65	1.92	2.59	5.74
LiBr	—	4.68	2.39	2.83	2.16	—	5.71
LiI	—	5.17	2.48	2.98	2.31	—	2.99
NaF	—	4.19	2.04	3.01	2.35	2.55	2.04
NaCl	**3.54**	4.25	2.67	3.39	2.72	2.99	5.64
NaBr	—	—	2.64	3.33	2.67	2.90	3.44
NaI	**3.27**	4.48	2.75	3.57	2.90	2.95	7.41
KF	—	—	2.46	3.02	2.35	3.08	1.00
KCl	—	4.31	2.36	3.45	2.79	3.48	3.46
KBr	—	4.38	2.83	3.65	2.99	4.43	4.36
KI	**3.85**	4.09	2.87	3.74	3.08	3.37	2.72
RbF	—	—	2.69	3.34	2.67	3.24	2.10
RbCl	**4.62**	4.35	2.87	3.78	3.11	3.60	4.06
RbBr	**4.48**	4.30	2.89	3.84	3.17	3.59	3.65
RbI	**4.41**	4.40	3.06	3.98	3.32	3.56	4.87
CsF	—	—	2.42	2.87	2.20	—	—
CsCl	—	—	3.03	4.14	3.48	—	—
CsBr	—	—	3.00	4.04	3.38	—	—
CsI	—	—	3.32	4.74	4.07	—	—

* Using Born-Mayer potential.

** Using compressibility data.

the results with other reported theoretical values it is found that the present results exhibit better agreement with experimental data than those of Kachhava and Saxena[24, 25] who used the Born-Mayer model (Col. 5) and Born model (Col. 4 and 6) and adopted a similar approach as has been employed in the present treatment. However, for lithium salts the values calculated[24] with the aid of B-M model (Col. 5) show a better agreement than the present results.

In Table 5 two sets of experimental values of δ have been given (Col. 2 and 3) which have been calculated[30] by feeding the observed data into two separate equations defining δ. A third experimental value obtained by doubling the experimental value of γ, following Chang's relationship[29], has also been reported for the sake of mutual comparison. Analogous to γ all the theoretical results regarding δ show a volume dependence in the sense that the value of δ for a crystal depends upon its size. A smooth variation of δ values may be observed with the change in the specific volume from crystal to crystal. In cesium halides, however, δ varies much more rapidly as compared to other crystals. The difference between the CsF and CsI values is considerably larger than for the fluorides and iodides of other metals. This type of behaviour is in agreement with the observed results and consequently may be attributed to the transformed geometry of the cesium crystals. It is clear from the Table that all the three calculated values of δ are in reasonable mutual agreement and are close to the experimental values as compared to those of Mathur and Singh[31] obtained using compressibility data (Col. 8) which show a very abrupt and irregular behaviour. In case of lighter crystals (LiX) and (NaX), however, the values of these authors[31] using a Mie-Grüneisen equation of state are comparable to the present results. It is worth mentioning that most relevent results for δ are obtained from Eq. (11), which is obvious due to the general character of the equation and the small number of approximations being involved in its derivation. A mutual comparison between the results obtained from the two equations of Chang[29] suggests that Eq. (12) suits for lighter crystals (halides of lithium and sodium) while for the rest Eq. (13) is a better choise.

It is evident from the analysis of the various results presented in the Tables that, except for the lithium salts, the modified V-S potential appears to be a good choise for explaining the behaviour of alkali halide lattices. Lithium salts are the lightest members in the whole family and, moreover, their cation-anion difference is considerable. An accurate information about the interionic forces in lithium salts should be sought through an appropriate approach – such as a logarithmic potential which suits especially to lighter ions. The Born-Mayer model yields best results for the halides having approximately equal anion and cation size.

It may be mentioned that the yield of anomolous results for frequency in case of fluorides is not the weakness of present model but is an inherent characteristic of rigid ion approach as a whole. No potential model based on rigid ion approach explains satisfactorily the behaviour of fluorides.

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