RESEARCH ARTICLE

COMPUTATION OF FORCE CONSTANT, LATTICE FREQUENCY AND DEBYE TEMPERATURE OF ALKALI HALIDE CRYSTALS ON THE BASIS OF TWO FORMS OF POTENTIAL ENERGY FUNCTIONS

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ABSTRACT

The force constant, lattice frequency and the Debye temperature of the ionic crystals have been computed for twenty alkali halides. These molecules are halides of Li, Na, K, Rb and Cs. The two forms of potential energy functions have been employed labeled as Woodcock model and L5 Model. A new relation for the estimation of force constant of diatomic crystals by using molecular constants data has also been developed. The variations of each property have been plotted and the comparative study has been done.

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INTRODUCTION

The interaction potential energy function has been a subject of extensive study for the last several decades for evaluating several properties of diatomic crystals. Several attempts [1-11] have been made to compute the values of force constant, cohesive energy, electron affinity, Debye temperature etc. of the ionic crystals on the basis of different forms of potential energy functions. Thakur and Pandey[12,13] have suggested three new potential energy functions which give improved potential energy and force curve for ionic crystals. The anharmonic interactions in solids have become the subject of a number of investigations [3,5,15,16] as they play very important role in explaining the various thermodynamic properties. In this connection, it is worthwhile to describe the single parameter theory, i.e Debye temperature (Θ_D) having ability to explain various characteristics of solids.

THEORETICAL FORMULATION

To compute the various properties of diatomic crystals, generalised pair potential proposed by Woodcock and logarithmic potential function have the following forms for the crystalline state

Woodcock potential[40] Model

$$U(r) = A \cdot r^{-m} \cdot e^{\wedge}[\{-B(r^n-1)\}] - (M.Z_1.Z_2.e^2)/r \qquad 1$$

Logarithmic (L5 Model) potential[41] model

$$U(r) = -m[\{(M.Z_1.Z_2.e^2)/r\} + G\log(1+g/r^n)] \qquad 2$$

Where U (r) is potential energy of an unlike ion pair in the crystal lattice interacting each other and with the rest of the lattice, M is Madelung constant, Z_1e and Z_2e are the charges on the ions, r is ionic separation and m, n, G , g are the constants known as potential parameters.

To compute one of the parameters-

$$U'(r_0) = 0 \qquad 3$$

Where U' (r) is the fiest derivative of U(r) and r_0 is the equilibrium nearest neighbour distance.

The comparative condition for evaluating the second potential parameters of the crystals given by-

$$U''(r_0) = 9 Cr_0/\beta \qquad 4$$

Where $U''(r_0)$ is second derivative of $U(r)$, C is crystal parameter and β is compressibility.

Applying the conditions, eq (3) and (4) yields the values

For Woodcock Model

$$A = Z_1 Z_2 M e^2 / [r_0^{(1-m)}. C. \exp \{ -B (r_0^n -1) \}.(m + n B r_0^n)] \qquad 5$$

$$B = [- X + \sqrt{(X^2 - 4YZ)}] / 2Y \qquad 6$$

Where

$$X = r_0^n [2mn - n^2 - nr_0 . \{(9Cr_0^3/ \beta)+ (Z_1 Z_2 Me^2/ r_0)\} / (Z_1 Z_2 Me^2)]$$
$$Y = n^2 r_0^{2n}$$

And $Z = m^2 - mr_0 \{(9Cr_0^3/ \beta)+ (Z_1 Z_2 Me^2/ r_0)\} / (Z_1 Z_2 Me^2)$

For L_5 Model

$$G = [M Z_1 Z_2 e^2 (r^{n+1} + g.r)] / r^2 ng \qquad 7$$

And $g = r_0^n . [n-1- \{9Cr_0^4 / (A Z_1 Z_2 e^2 m \beta)\}] / [1+ \{9 Cr_0^4 / (A Z_1 Z_2 e^2 m \beta)\}] \qquad 8$

Where m and n are used for simplification and given by

$$m = 1 + (1.6 e^2 / k_e r_e^3) \text{ and } n = 0.6 + (k_e r_e^3 / e^2 m)$$

The values of r_0 have been taken from the work of Das and Saxena[45]. Due to unavailability of the experimental values of compressibility, it has been calculated using the following expression based on modified Gaussian potential energy function[46-48]. A detailed theoretical evaluation of β has been given by Mitra and Joshi[5]. The final expression for β is,

$$\beta = 9Cr_0^4 / \{e^2 Z^2 (3/2) k r_0^{3/2} - (5/2) \} \qquad 9$$

Force constant – The potential energy per ion-pair in diatomic crystals is

$$\Phi_{(x)} = \Phi_{(0)} + f.x^2 + a. x^4 +….. \qquad 10$$

Where $x \ll r_0$ and $\Phi_{(0)}$ refers to the value of $\Phi_{(x)}$ at x=0 and numerically equal to $\Phi_{(r_0)}$.

The coefficient x^4 and x^2 determine respectively the anharmonicity and frequency of oscillation of the crystals. The terms involving odd power in x in eq. (10) are absent due to the existence of the centre of symmetry of lattice points in these crystals.

Following Krishnan and Roy[3], the force constant (f) which is the coefficient of Δr, the change in internuclear distance in the expression for $d\Phi_r / dr$ is given by

$$f = 1/3 [\Psi'' r_0 + (2/r_0) \Psi'(r_0)] \qquad 11$$

On applying the relation (11) to eq (1) and (2),

$$f = [M e^2 Z_1 Z_2 \{ (2mn - n^2 + n)Br_0^n + n^2 B^2 r_0^{2n} + m^2 - m \}] / \{ 3 r_0^3 (m + nBr_0^n) \} \qquad 12$$

$$f = [mM Z_1 Z_2 e^2 \{ (n-1)r_0^n - g \}/ 3 r_0^3 (r_0^n + g) \} \qquad 13$$

Lattice frequency and Debye temperature

The infra-red frequency ν is

$$\nu = \frac{1}{2\pi} \sqrt{(\frac{f}{\mu})} , \text{ where f is force constant and μ is reduced mass.} \qquad 14$$

The Debye temperature, $\Theta_D = h\nu / k \qquad 15$

where h is Planck's constant and k is the Boltzmann constant. New proposed method- A simple relation for the estimation of force constant of diatomic rystals by using molecular constants data is developed. In eq. (1) and (2), A, B, G, g respectively are the potential parameters. These parameters can be determined by using the following molecular stability and force constant conditions

$$U' (r_e) = 0 \qquad 16$$

$$U'' (r_e) = k_e \qquad 17$$

Where r_e is intern clear distance.

For the determination of force constant, eq. (11) has been modified using Krishnan and Roy approach[3].

$$f = 2/3 [\Psi'' r_0 + (2/r_0) \Psi'(r_0)] \qquad 18$$

where $\Psi'(r_0)$ and $\Psi'' r_0$ are non-electrostatic part of U(r). This procedure eventually allows to easily evaluate unknown force constant from molecular constants like r_e and k_e and the results have been compared with the corresponding values reported in literature.

RESULTS AND DISCUSSION

The force constant, lattice frequency and Debye temperature of the ionic crystals on the basis of two forms of potential energy functions have been computed for twenty alkali halides. The experimental values of various parameters, Madelung constant (M), the crystal parameter (C), equilibrium nearest neighbour distance (r_0) and compressibility (β) have been taken from the work of Pandey[51] and Born and Huang[42]. The two potential forms are (1) and (2) labelled as Woodcock and L_5 models are used for calculation.
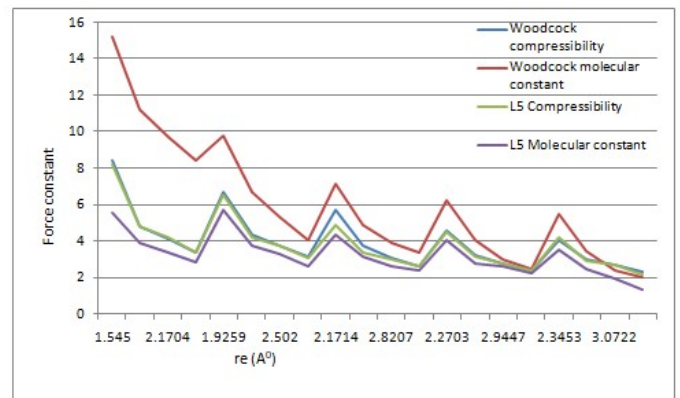

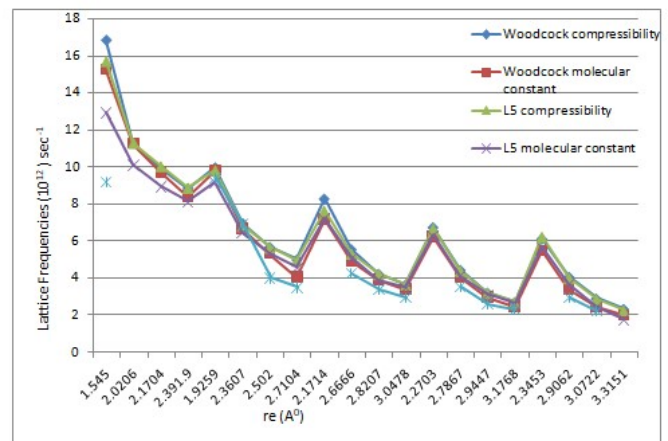**Fig.1. Force constants (f) of alkali halide crystals**

Fig.2. Lattice frequencies ($10^{12} sec^{-1}$) of alkali halide crystals

Table 1. Comparison of calculated and experimental values of force constant (f) of alkali halide crystals from different sources

		Force constant (f)			
		Woodcock		L5 Model	
Molecule	Re (A°)	Compressibility	Molecular constants	Compressibility	Molecular constants
LiF	1.545	8.45	15.21	8.23	5.6
LiCl	2.0206	4.86	11.24	4.86	3.9
LiBr	2.1704	4.15	9.7	4.23	3.37
Lil	2.3919	3.4	8.41	3.4	2.86
NaF	1.9259	6.75	9.8	6.6	5.72
NaCl	2.3607	4.4	6.66	4.26	3.76
NaBr	2.502	3.77	5.31	3.77	3.33
Nal	2.7104	3.19	4.05	3.13	2.66
KF	2.1714	5.72	7.17	4.92	4.33
KCl	2.6666	3.74	4.9	3.43	3.12
KBr	2.8207	3.07	3.92	3.06	2.59
Kl	3.0478	2.62	3.41	2.62	2.37
RbF	2.2703	4.61	6.23	4.54	4.05
RbCl	2.7867	3.21	4.02	3.2	2.76
RbBr	2.9447	2.8	2.98	2.79	2.62
Rbl	3.1768	2.4	2.47	2.45	2.27
CsF	2.3453	4.08	5.47	4.24	3.5
CsCl	2.9062	3	3.42	2.95	2.48
CsBr	3.0722	2.75	2.43	2.74	1.93
Csl	3.3151	2.34	2.02	2.2	1.34

Table 2. Comparison of calculated and experimental values of lattice frequency (ν) of alkali halide crystals from different sources

		Lattice frequency (ν) in 10^{12} sec^{-1}				
		Woodcock		L5 Model		
Crystal	Re (A°)	Compressibility	Moleular constants	Compressibility	Molecular constants	Experimental
LiF	1.545	16.8	15.21	15.7	12.91	9.21
LiCl	2.021	11.27	11.24	11.3	10.08	-
LiBr	2.17	9.91	9.7	10.04	8.93	-
Lil	2.3919	8.83	8.41	8.87	8.1	-
NaF	1.926	9.95	9.8	9.83	9.16	9.4
NaCl	2.361	6.96	6.66	6.82	6.43	6.91
NaBr	2.502	5.68	5.31	5.66	5.34	4.02
Nal	2.71	5.01	4.05	4.94	4.56	3.51
KF	2.171	8.27	7.17	7.66	7.18	-
KCl	2.667	5.56	4.9	5.33	5.08	4.25
KBr	2.821	4.24	3.92	4.22	3.89	3.4
Kl	3.048	3.67	3.41	3.66	3.48	2.94
RbF	2.27	6.74	6.23	6.68	6.3	-
RbCl	2.787	4.45	4.02	4.41	4.12	3.54
RbBr	2.945	3.23	2.98	3.21	3.13	2.63
Rbl	3.177	2.71	2.47	2.7	2.61	2.32
CsF	2.345	6.12	5.47	6.24	5.66	-
CsCl	2.906	4.07	3.42	4.01	3.68	2.94
CsBr	3.072	2.91	2.43	2.89	2.44	2.24
Csl	3.315	2.35	2.02	2.28	1.77	-

Table 3. Comparison of calculated and experimental values of Debye temperature (Θ_D) of alkali halide crystals from different sources

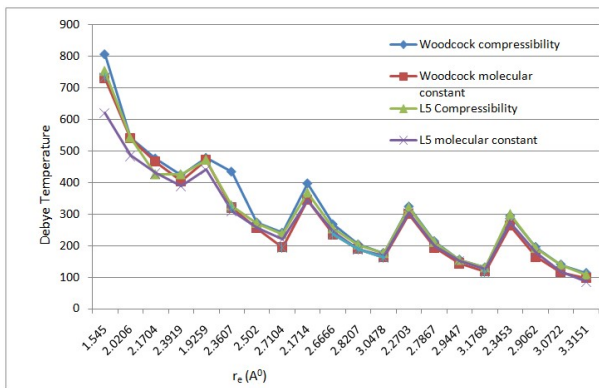|		Debye temperature Θ_D in (^{0}K)				
		Woodcock		L5 Model		
Crystal	Re (A°)	Compressibility	Molecular constants	Compressibility	Molecular constant	Experimental
LiF	1.545	806.5	730.71	753.46	620.09	732
LiCl	2.021	540.7	539.87	542.3	484.56	-
LiBr	2.17	475.8	466.11	425.83	429.26	-
Lil	2.392	423.9	404.17	425.68	389.38	-
NaF	1.926	477.7	471.07	471.75	440.14	-
NaCl	2.361	434	320.11	327.3	308.98	321
NaBr	2.502	272.8	255.36	271.63	256.62	-
Nal	2.71	240.3	194.57	237.07	219.15	195
KF	2.171	396.8	344.71	367.61	344.12	-
KCl	2.667	267.1	235.61	254.35	244.26	236
KBr	2.821	203.4	188.38	202.52	186.87	188
Kl	3.048	176.1	163.83	175.64	167.14	163
RbF	2.27	323.4	299.41	321	302.94	-
RbCl	2.787	213.4	193.18	211.64	198.17	-
RbBr	2.945	155.2	143.14	154.05	150.16	-
Rbl	3.177	130.1	118.46	130	125.28	115
CsF	2.345	293.8	262.72	299.48	272.16	-
CsCl	2.906	195.3	164.45	192	177	-
CsBr	3.072	139.7	116.8	138.69	117.12	-
Csl	3.315	112.6	97.13	107.5	85.23	-

Fig. 3. Debye temperature (Θ_D) of alkali halide crystals

The variations of force constant with r_e (A^0) has been plotted for all the four different types of approaches and the result seems to be quite reasonable. The variation of lattice frequency with r_e (A^0) shows that values obtained from Woodcock potential based on modified approach and using molecular constants are in excellent agreement with the available experimental data. The variation of Debye temperature shows that Woodcock and experimental data have comparable slopes of -44.79 and -54.01 respectively. In view of the uncertainties in the values of r_0 and β and the approximation inherent theory, the calculated values of Θ_D appear to agree quite well. The Woodcock model gives the best agreement with the experimental values. In this connection, potential eq.(1) seems to the best function for the crystals as the same results were given in the case of Debye temperature. Thus the validity of the newly proposed relation in the calculation of Θ_D has been justified.

CONCLUSION

The nature of binding in diatomic crystals has been a subject of study for the last several years. Woodcock and newly proposed logarithmic potential functions yield acceptable behaviour of the potential energy for diatomic crystals. Hence, we computed the various properties of crystalline state namely, force constant, lattice frequency and the Debye temperature. The theoretical results obtained in the present study indicate that all the Woodcock potential yield better agreement with the experimental values. The comparative study of both methods viz. compressibility data and molecular constants advocates the validity newly proposed force constant relation based on molecular constants. Our calculated values are in reasonably good agreement with corresponding experimental data. The present study also supports existence of the relation between crystal parameter and molecular constants. This study could act as a guide for developing some more general correlations.

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