Second Order Elastic Constants and Some Thermoelastic Properties of Alkali Halides Using WOODCOCK Potential

Harun Reşit YAZAR
Department of Physics, Kırıkkale University,
71450, Yahşihan, Kırıkkale-TURKEY
Sedat AĞAN
Department of Physics, The University of Warwick,
Coventry, CV4 7AL-UK
Kemal ÇOLAKOĞLU
Department of Physics, Gazi University,
06500, Ankara-TURKEY

Abstract

Second Order Elastic Constants (S.O.E.C) of NaCl-type crystals have been calculated using the Woodcock potential. Short-range repulsive interactions have been included up to second-nearest neighbors. This potential form represents the composite form of the inverse power dependence and exponential dependence of the repulsive energy on interionic distance. Some thermoelastic and thermodynamic properties such as Anderson-Grüneisen parameters δ_T, and δ_S, Volume thermal expansion coefficient β and Grüneisen gama γ_G have been calculated in terms of calculated values of S.O.E.C and Third Order Elastic Constant (T.O.E.C).

Key Words: Second order elastic constant, NaCl-type crystal, Anderson-Grüneisen.

1. Introduction

The quantum mechanical calculation of the repulsive energy of a pair of multielectron atoms or ions is an extremely difficult and complicated task even for simple condensed systems of closed shell ions such as NaCl-like alkali halides. Semiempiracal and phenomenological potential forms have therefore been developed which represent the exponential dependence on interionic distance such as the Born-Mayer exponential form, and

the inverse power dependence as the Born-Lande inverse power form. Studies on the alkali halides provide a critical test of different interionic potentials. Woodcock proposed [1] a composite form for the repulsive interaction energy and demostrated its applicability in alkali halide moleculs and crystals by calculating the binding energy and compressibility. In the present paper we investigate the applicability of Woodcock potential by calculating S.O.E.C and some physical quantities such as Anderson-Grüneisen parameters δ_T, δ_S, volume thermal expansion coefficient β and Grüneisen gama γ_G have been calculated in terms of S.O.E.C and T.O.E.C [2].

Theory and method of calculation are given in the following section 2.

2. Theory and Method of Calculation

For an ionic crystal, the effective pair potential φ (r) can be written as [3],

$$\varphi(r) = -\frac{\alpha_M e^2}{r} + \frac{B}{r^n} \exp\left(-\frac{r^m}{\rho}\right) - \frac{C}{r^6} - \frac{D}{r^8}, \tag{1}$$

where r is the interionic distance. The first term on the right handside of (1) represents the long-range electrostatic Madelung energy term, second term represents the short-range overlap repulsive interaction, and the last two terms represent the Van Der Waals dipole-dipole and dipole-quadropole interactions. We take n=4 and m=1 so that

$$\varphi(r) = -\frac{\alpha_M e^2}{r} + \frac{B}{r^4} \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6} - \frac{D}{r^8}. \tag{2}$$

This choice of pair potential is simple and preferable over others mainly because such simple exponentials as in the overlap repulsive potential Eq.(2) also appear in the Heitler-London calculations for the hydrogen molecule. Moreover, the factor r^{-4} takes proper account of the polorization energy term [4]. The repulsive parameters are calculated from the usual method based on the equation of state and ultrasonic data [5].

2.1. Elastic Constants

The derivative of the potential energy ϕ for central forces are most conveniently expressed in spherical coordinates. The transformation from rectangular to spherical coordinates is given by [6]

$$\left(\frac{\partial \phi}{\partial \alpha}\right)_r = \alpha P \tag{3}$$

$$\left(\frac{\partial^2 \phi}{\partial \alpha \partial \beta}\right)_r = \delta_{\alpha\beta} P + \alpha\beta Q, \tag{4}$$

where

$$P = \left(\frac{1}{r}\frac{\partial \phi}{\partial r}\right); \tag{5}$$

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$$Q = \left[\frac{1}{r} \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial \phi}{\partial r} \right) \right]; \tag{6}$$

$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ and $\alpha \equiv \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V$ are mechanical coefficients of releated materials; and

$$\delta_{\alpha\beta} = \left\{ \begin{array}{l} 1 \text{ for } \alpha = \beta \\ 0 \text{ for } \alpha \neq \beta. \end{array} \right.$$

The equations for the elastic constants are then those as defined by Anderson [7] where Δ is the volume-per cell (ion pair).

$$C_{11} = (C_{xx,xx}) = \frac{1}{\Delta} \sum_l \left\{ Q \left(x^l \right)^4 + P \left(x^l \right)^2 \right\}, \tag{7}$$

$$C_{22} = (C_{xx,yy}) = \frac{1}{\Delta} \sum_l \left\{ Q \left(x^l \right)^2 \left(y^l \right)^2 - P \left(x^l \right)^2 \right\}, \tag{8}$$

$$C_{44} = (C^*_{xy,xy}) = \frac{1}{\Delta} \sum_l \left\{ Q \left(x^l \right)^2 \left(y^l \right)^2 + P \left(x^l \right)^2 \right\}. \tag{9}$$

S.O.E.C. have been obtained from transportation of cartesian coordinates to spherical coordinates system and given in Table 1. Since forces are additive the derivative of the potential in the equations of motion are additive, and the elastic constants can be broken down into a sum;

$$(C_{\alpha\beta,\gamma\lambda}) = (C_{\alpha\beta,\gamma\lambda})^e + (C_{\alpha\beta,\gamma\lambda})^R. \tag{10}$$

Table 1. S.O.E.C. have been obtained from transportation of cartesian coordinates to spherical coordinates system.

	NaCl-Structure
$\Delta\ C_{11}^R$	$2Q^R r^4 + 2P^R r^2$
$\Delta\ C_{12}^R$	$-2P^R r^2$
$\Delta\ C_{44}^R$	$2P^R r^2$

The reason these constants are broken down into two parts is that the sum motion is taken to infinity for the e component (standing for the electrostatic or Coulombic interaction), while the summation is taken only over nearest neighbors for R component (R standing for repulsive). This separation corresponds to the separate parts of the lattice potential arising between the k and k' positions which is appropriate to define the energy per unit cell:

$$\phi_{kk'} = -\frac{A_r Z_k Z_{k'} e^2}{r_{kk'}} + M_k V(r). \tag{11}$$

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Where M_k is the coordination number around the k position. For the case of NaCl, $M_k=6$. A_r is the madelung constant of the lattice, Z_k and $Z_{k'}$ are the valence number and e, is the electronic charge and V(r) is the repulsive potential.

Denoting the potential above by the symbols R and e corresponding to the two terms in Eq.(11), we write,

$$\phi = \phi^e + \phi^R. \tag{12}$$

Also denote the operators P and Q by the same symbols so that

$$P^R = \frac{1}{r}\left(\frac{\partial \phi^R}{\partial r}\right)_r \quad \text{and} \quad Q^R = \left[\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial \phi^R}{\partial r}\right)\right]_r \tag{13}$$

with the elastic constants (for example C_{11}) related as

$$C_{11} = C_{11}^e + C_{11}^R. \tag{14}$$

Repulsive parts of the elastic constant (for example C_{11}^R) can be expressed in terms of P^R and Q^R operators and are given in Table 1. It's clearly seen from Equation (13) that P^R and Q^R can be written as a first and second derivative of the potential and these forms are given in Table 2. The madelung constants can be defined two ways:s a constant A_r corresponding to the nearest-neigbor distance r, or A_a corresponding to half distance a of the unit cell. For comparison purposes, set $A_r = A_a$ for NaCl and $A_a = \frac{\sqrt{3}}{3} A_r$ for CsCl. Similarly, r = a for NaCl, and a $= \frac{\sqrt{3}}{3}$r for CsCl.

Table 2. The elastic constant parameters in terms of the derivatives of the repulsive potential [V(r)].

	NaCl-Structure
$\Delta\ C_{11}^R$	$2r^2 d^2 V/dr^2$
$\Delta\ C_{12}^R$	$-2r(dV/dr)$
$\Delta\ C_{44}^R$	$2r(dV/dr)$

2.2. The Short-range component of the potential

We now express the operators P and Q in terms of the derivatives of the repulsive potential with respect to r. It is readily seen that,

$$Q^R = \frac{1}{r^2}\frac{d^2V}{dr^2} - \frac{1}{r^3}\frac{dV}{dr} \quad \text{and} \tag{15}$$

$$P^R = \frac{1}{r}\frac{dV}{dr}. \tag{16}$$

In tabular form, the results are given in Table 2.

There are two ways to proceed from this point. One way is to represent the operators d^2V/dr^2 and dV/dr at the equlibrium condition r $= r_0$ as pure numbers and then evaluate

the numbers from experiments on the elastic constants. The second way is to assume some function through the operators. We will proceed with the elastic constants as function of r.

Let us take the repulsive potential as

$$V(r) = \frac{B}{r^4} e^{-\frac{r}{\rho}}, \tag{17}$$

where B and ρ are potential parameters which have been calculated from Ref.[8]. Using Equation (17) in Table 2, we have evaluated the repulsive term in the elastic constants in terms of this potential in Table 3.

Table 3. The elastic constant parameters in terms of the Woodcock potential.

	NaCl-Structure
C_{11}^R	$\frac{1}{2M} \frac{A_r Z^2 e^2 \rho}{(4\rho+r)} \left(\frac{40\rho^2 + 7\rho r + r^2}{\rho^2 r^4} \right)$
$C_{1\ 2}^R$	$\frac{A_r Z^2 e^2}{r^3 M (4\rho+r)} + \frac{4 A_r Z^2 e^2 \rho}{r^4 M (4\rho+r)}$
C_{44}^R	$-\frac{A_r Z^2 e^2}{r^3 M (4\rho+r)} - \frac{4 A_r Z^2 e^2 \rho}{r^4 M (4\rho+r)}$

With the derivative of Equation (11) vanishing at equilibrium, r = r$_0$. Thus

$$\frac{4Be^{-\frac{r}{\rho}}}{r^5} + \frac{Be^{-\frac{r}{\rho}}}{\rho r^4} = \frac{A_r Z^2 e^2}{Mr^2} \tag{18}$$

and

$$P^R = -\frac{Be^{-\frac{r}{\rho}}}{\rho r^5} - \frac{4Be^{-\frac{r}{\rho}}}{r^6} \tag{19}$$

$$Q^R = \frac{24Be^{-\frac{r}{\rho}}}{\rho r^8} + \frac{9Be^{-\frac{r}{\rho}}}{\rho r^7} + \frac{Be^{-\frac{r}{\rho}}}{\rho^2 r^6}. \tag{20}$$

The elastic constants expressions can be obtained by combining the results shown in Table 4 with those in Table 3. The full expressions for the elastic constants are (for NaCl-structure)

Table 4. Values of lattice sum for the coulombic potential. The units of C_{ij} are $Z^2 e^2 / \Delta a$ where Δ is the volume of the cell.

	NaCl-Structure
A_a	1.74756
A_r	1.74756
$C^e_{\ 11}$	-2.55604
$C^e_{\ 12}$	0.11298
$C^e_{\ 44}$	1.27802

$$C_{11} = \frac{1}{2M} \frac{A_r Z^2 e^2 \rho}{(4\rho + r)} \left(\frac{40\rho^2 + 7\rho r + r^2}{\rho^2 r^4} \right) - 2.55604 \frac{Z^2 e^2}{\Delta_0 a_0} \qquad (21)$$

$$C_{12} = \frac{A_r Z^2 e^2}{r^3 M(4\rho + r)} + \frac{4 A_r Z^2 e^2 \rho}{r^4 M(4\rho + r)} \quad + \quad 0.11298 \frac{Z^2 e^2}{\Delta_0 a_0} \qquad (22)$$

$$C_{44} = -\frac{A_r Z^2 e^2}{r^3 M(4\rho + r)} - \frac{4 A_r Z^2 e^2 \rho}{r^4 M(4\rho + r)} \quad + \quad 1.27802 \frac{Z^2 e^2}{\Delta_0 a_0}. \qquad (23)$$

Calculated values of S.O.E.C and Experimental values [9] are given in Table 5.

Table 5. Calculated values of S.O.E.C and Experimental values [12].

	$C_{11} \times 10^{11}$ dyn/cm^2 This Work	$C_{11} \times 10^{11}$ dyn/cm^2 [9] Experiment	$C_{12} \times 10^{11}$ dyn/cm^2 This Work	$C_{12} \times 10^{11}$ dyn/cm^2 [9] Experiment	$C_{44} \times 10^{11}$ dyn/cm^2 This Work	$C_{44} \times 10^{11}$ dyn/cm^2 [9] Experiment
LiF	11.95	11.04	5.04	4.43	5.04	6.36
LiCl	4.21	4.94	1.92	2.28	1.92	2.46
LiBr	3.54	3.94	1.47	1.87	1.47	1.93
LiI	2.84	2.85	1.05	1.40	1.05	1.35
NaF	8.50	9.45	2.88	2.12	2.88	2.82
NaCl	4.79	4.79	1.26	1.15	1.26	1.27
NaBr	4.23	4.01	1.05	1.09	1.05	0.99
NaI	3.71	3.03	1.05	0.88	1.05	0.74
KF	5.81	6.56	1.63	1.46	1.63	1.25
KCl	3.75	3.98	0.84	0.61	0.84	0.63
KBr	3.31	3.35	0.70	0.45	0.70	0.50
KI	2.69	2.67	0.54	0.40	0.54	0.36
RbF	5.06	5.53	1.32	1.40	1.32	0.93
RbCl	3.32	3.63	0.71	0.62	0.71	0.47
RbBr	2.94	3.15	0.59	0.49	0.59	0.38
RbI	2.48	2.54	0.46	0.40	0.46	0.27

2.3. Thermoelastic Quantities γ_G, δ_T, δ_S and β

It is possible to obtain expressions for thermoelastic quantities such as γ_G, δ_T, δ_S and volume thermal expansion coefficient β in terms of S.O.E.C and T.O.E.C. This approach has been applied by Rao [10] for metals and a non-metallic crystal. Useful expressions are as follows [8]:

$$\delta_S = -\frac{B_T}{B_S}\left[2T\beta\gamma + \frac{C_{111} + 6C_{112} + 2C_{123}}{3(C_{11} + 2C_{12})}\right] - \frac{1}{\beta}\left(\frac{\partial \ln B_S}{\partial T}\right)_V \tag{24}$$

$$\delta_T = -\frac{C_{111} + 6C_{112} + 2C_{123}}{3(C_{11} + 2C_{12})} - \frac{1}{\beta}\left(\frac{\partial \ln B_T}{\partial T}\right)_V \tag{25}$$

$$\beta = -\frac{C_V}{2V(C_{11} + 2C_{12})^2}\left[3\left(C_{11} + 2C_{12}\right) + \left(C_{111} + 6C_{112} + 2C_{123}\right)\right], \tag{26}$$

$$\gamma_G = -\frac{1}{3} - \frac{V}{2}\frac{P1}{P2} \tag{27}$$

where P1 and P2 are given in terms of the elastic constants as follows:

$$P1 = \frac{dP}{dV} = -\frac{1}{3V}[C_{11} + 2C_{12}] \tag{28}$$

$$P2 = \frac{d^2P}{dV^2} = \frac{1}{9V^2}[3(C_{11} + 2C_{12}) - (C_{111} + 6C_{112} + 2C_{123})]. \tag{29}$$

Where B_T, B_S and C_V refers to isothermal-adiabatic bulk modulus and specific heat at constant volume, respectively. B_T, B_S, C_V and $\frac{1}{\beta}\left(\frac{\partial \ln B_S}{\partial T}\right)_V$ are taken from literature [11]. Third order elastic constants are taken from [12]. Both experimental (taken from ref.[13]) and calculated values of the thermoelastic Quantities γ_G, δ_T, δ_S and β in terms of S.O.E.C and T.O.E.C. are given in Table 6.

Table 6. Thermoelastic Quantities γ_G , δ_T, δ_S and β in terms of S.O.E.C and T.O.E.C.

	β $(10^{-4}\mathrm{K}^{-1})$ This work	β $(10^{-4}\mathrm{K}^{-1})$ Theory(1) [14]	β $(10^{-4}\,\mathrm{K}^{-1})$ Theory(2) [14]	β $(10^{-4}\mathrm{K}^{-1})$ Experiment [13]	δ_S (10^{-4}) This work	δ_S (10^{-4}) Theory(1) [14]	δ_S (10^{-4}) Theory(2) [14]	δ_S (10^{-4}) Experiment [13]
LiF	0.84	0.86	1.03	0.99	2.32	4.70	5.27	3.56
LiCl	1.77	1.16	1.37	1.32	3.89	5.58	6.20	4.09
LiBr	1.95	1.25	1.48	1.50	4.18	5.93	6.57	4.12
LiI	1.82	1.47	1.83	1.80	2.32	5.45	6.23	4.06
NaF	0.86	1.14	1.37	0.96	2.24	4.52	5.13	3.75
NaCl	1.10	1.29	1.49	1.19	2.49	5.25	5.83	3.80
NaBr	1.30	1.40	1.63	1.26	3.44	5.53	6.15	4.11
NaI	0.81	1.55	1.85	1.37	2.44	5.46	6.14	4.13
KF	1.07	1.27	1.50	1.02	3.06	5.21	5.84	4.08
KCl	1.33	1.41	1.65	1.11	3.69	5.61	6.23	4.38
KBr	1.46	1.45	1.68	1.16	3.68	5.38	6.01	4.02
KI	1.73	1.56	1.81	1.23	4.08	5.18	5.84	3.93
RbF	1.32	1.27	1.48	0.94	4.33	5.77	6.38	4.97
RbCl	1.67	1.39	1.59	1.03	5.08	6.33	6.93	4.93
RbBr	1.57	1.47	1.69	1.08	4.57	6.14	6.76	4.72
RbI	1.72	1.52	1.75	1.23	4.66	6.24	6.87	4.47

Table 6. (continue)

	δ_T (10^{-4}) This wor	δ_T (10^{-4}) Theory (1) [14]	δ_T (10^{-4}) Theory (2) [14]	δ_T (10^{-4}) Experiment [13]	γ_G This wor	γ_G Theory (1) [14]	γ_G Theory (2) [14]	γ_G Experiment [13]
LiF	4.74	2.38	2.95	6.00	1.52	1.47	1.75	1.63
LiCl	6.66	3.29	3.90	6.77	2.22	1.68	1.98	1.81
LiBr	7.19	3.59	4.23	7.01	2.34	1.75	2.07	1.94
LiI	6.40	2.91	3.69	7.32	2.11	1.59	1.98	2.19
NaF	4.24	2.78	3.39	5.77	1.36	1.50	1.81	1.51
NaCl	4.51	3.41	4.00	5.85	1.52	1.87	2.16	1.61
NaBr	5.45	3.72	4.34	6.23	1.83	1.84	2.16	1.64
NaI	4.51	3.68	4.37	6.43	1.33	1.80	2.14	1.71
KF	5.02	3.46	4.09	6.20	1.59	1.69	2.00	1.52
KCl	5.49	3.93	4.55	6.22	1.87	1.89	2.20	1.49
KBr	5.46	3.82	4.45	5.88	2.02	1.97	2.29	1.50
KI	5.89	3.74	4.40	5.76	2.34	1.99	2.32	1.53
RbF	5.96	4.40	5.01	6.80	1.92	1.83	2.14	1.40
RbCl	6.79	4.85	5.44	6.76	2.32	2.07	2.37	1.39
RbBr	6.32	4.66	5.28	6.60	2.15	2.05	2.36	1.42
RbI	6.61	4.66	5.29	6.52	2.34	2.15	2.46	1.56

3. Results and Discussion

In this work, the applicability of the Woodcock potential is considered for studying the crystalline properties of alkali halides. This potential form represents the composite form of the inverse power dependence and the exponential dependence of the repulsive energy

Second order elastic constants are calculated using Woodcock potential and compared with the experimental data and some other theoretical works. Some physical quantities such as Anderson-Grüneisen parameters (δ_T, δ_S), volume thermal expantion coefficient (β) and Grüneisen gamma (γ_G) are calculated in terms of S.O.E.C and T.O.E.C. Our calculated values of volume thermal expansion coefficients of sixteen NaCl-structure alkali halide crystals have been obtained more reasonable agreements with the experimental data than the Theory (1) and Theory (2)[14].The obtained results from the structure of LiF,LiI,NaF,NaCl,NaBr,KF,KCI and KBr are in good agreement than the Theory (1) and Theory (2). However , Theory (1) and Theory (2) give more reasonable agreement with the experimental data for the structures of LiCI,LiBr,NaI,KI and Rubidium halides. From the structure of KBr,KI and Rubidium halides, the calculated values of δ_S gave good results but the other sixteen NaCl-structures could not be obtained. From the structure of LiCl,LiBr,KBr,KI,RbCl and RbI, the calculated values of the δ_T gave good results than the Theory (1) and Theory (2). Moreover, good results from the structure of LiI,NaF,NaCl,NaBr,KF and KCl were obtained for the Grüneisen gammas. We believe that different forms of potentials should be tested in order to understand the exact nature of the interionic interactions in the alkali halide systems.

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