

Interatomic forces, Grüneisen and Anderson-Grüneisen parameters of ionic crystals

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Abstract. The general expression for the Anderson-Grüneisen parameter δ recently derived by Gupta and others, has been used to study the variation of δ with the Grüneisen parameter γ employing the interaction approach. For this purpose four potential energy functions have been selected. It is found that δ values evaluated by the modified Varshni-Shukla potential are better than other forms of overlap repulsive interaction. The variation of δ with γ is also studied by plotting curves between δ and γ . The method of least-squares has been employed to yield the best fitted equation.

Keywords. Interatomic forces; Anderson-Grüneisen parameter; Grüneisen parameter; potential energy function.

1. Introduction

The Anderson-Grüneisen parameter δ is an important physical parameter which not only yields information about interatomic forces but predicts the macroscopic behaviour of different thermodynamic properties. Several authors (Anderson 1966, 1967; Chang 1967; Anderson *et al* 1968; Mathur and Singh 1968; Sharma and Tripathi 1972, 1973a, b, 1975; Sharma *et al* 1974) have studied δ for some ionic crystals. Anderson (1967) applied this parameter to solve certain geophysical and astrophysical problems. The dependence of δ on the temperature and pressure has been emphasised by Sharma and Gupta (1975). In the present paper, the general expression for δ recently developed by Gupta *et al* (1978) for some ionic crystals has been studied by employing the interaction approach. This approach can be directly applied to any form of potential energy function.

2. Theory

The parameter δ is generally expressed as

$$\delta = (\partial \ln \beta_s / \partial \ln V)_p, \quad (1)$$

where β_s is the adiabatic compressibility and V , the volume of the crystal.

The macroscopic theory of the temperature-dependent equation of state of solids leads to the Grüneisen parameter γ of the form

$$\gamma = - (d \ln \omega / d \ln V), \quad (2)$$

where ω is the angular frequency of vibration. Using Hildebrand's lattice condition and taking $\beta_s \approx \beta_T$ (isothermal compressibility) (Madan 1971a, b; Sharma and Tripathi 1973a, b; Sharma 1977), we obtain

$$\left(\frac{1}{\beta_s} \frac{d\beta_s}{dr} \right) = \frac{1}{r} \left[1 - \frac{r\psi'''(r)}{\psi''(r)} \right], \quad (3)$$

where r is the interionic distance; $\psi''(r)$ and $\psi'''(r)$ are the second and third derivatives of the potential energy function $\psi(r)$ with respect to r . Considering the expression for force-constant f as derived by Krishnan and Roy (1951), the reststrahlen angular frequency ω can be written as:

$$\omega^2 = \frac{1}{3\mu} \left[\phi''(r) + \frac{2}{r} \phi'(r) \right] = \frac{f}{\mu}, \quad (4)$$

where μ is the reduced mass per ion-pair; $\phi'(r)$ and $\phi''(r)$ are the first and the second derivative of $\phi(r)$ (short-range interaction energy term) with respect to r respectively. Following Sharma (1977), a general expression for δ may be derived as

$$\delta = \frac{2\gamma}{r} \left[\frac{r\psi'''(r)}{\psi''(r)} - 1 \right] \left[\frac{\phi''(r) + (2/r)\phi'(r)}{\phi'''(r) + (2/r)\phi''(r) - (2/r^2)\phi'(r)} \right]. \quad (5)$$

Recently the Grüneisen parameter γ has been expressed (Misra and Sharma 1972; Sharma and Jain 1973) in terms of the derivatives of the potential energy function as:

$$\gamma = - \frac{r}{6} \frac{\psi'''(r)}{\psi''(r)}. \quad (6)$$

Using (5) and (6), we can also write

$$\delta = - (2\gamma/r) (6\gamma + 1) \left[\frac{\phi''(r) + (2/r)\phi'(r)}{\phi'''(r) + (2/r)\phi''(r) - (2/r^2)\phi'(r)} \right]. \quad (7)$$

Equation (7) is used to compute δ values for alkali halides employing the four well-established potential energy functions *viz.* Börn, Börn-Mayer, Lennard-Jones (12 : 6) and the modified Varshni-Shukla. The potential energy per ion-pair of an ionic crystal is generally expressed as:

$$\psi(r) = - (\alpha e^2/r) + \phi(r), \quad (8)$$

where α is the Madelung constant and $\phi(r)$ is the short-range interaction energy which includes the overlap interaction energy, the dipole-dipole interaction energy, the dipole-quadrupole interaction energy and the zero-point energy.

For the Börn, Börn-Mayer, Lennard-Jones (12 : 6) and modified Varshni-Shukla potential equation (8) can be written respectively as

$$\psi(r) = -\frac{\alpha e^2}{r} + \frac{A}{r^n} - \frac{C}{r^6} - \frac{D}{r^8} + \epsilon_0, \quad (9)$$

$$\psi(r) = -\frac{\alpha e^2}{r} + B \exp(-r/\rho) - \frac{C}{r^6} - \frac{D}{r^8} + \epsilon_0, \quad (10)$$

$$\psi(r) = -\frac{\alpha e^2}{r} + \frac{\lambda}{r^{12}} - \frac{C}{r^6} - \frac{D}{r^8} + \epsilon_0, \quad (11)$$

$$\text{and } \psi(r) = -\frac{\alpha e^2}{r} + \sigma \exp(-br^{3/2}) - \frac{C}{r^6} - \frac{D}{r^8} + \epsilon_0, \quad (12)$$

where A , n , B , ρ , λ , σ and b are the potential parameters of the respective potentials, C and D are the van der Waal's constants and ϵ_0 the zero point-energy.

The potential parameters of equations (9), (10) and (12) have been evaluated employing the following well-known equilibrium conditions due to Hildebrand (1932)

$$\psi(r) = -E, \quad (13)$$

$$\text{and } \psi'(r) = 3vT\alpha_v/\beta_T r, \quad (14)$$

where E is the cohesive energy, T the temperature; α_v the coefficient of volume expansion, β_T the isothermal compressibility and v the volume of the unit cell. The parameter λ of equation (11) has been evaluated using the lattice condition given by (14). The computed values of the potential parameters are given in table 1. Once the potential parameters are evaluated, we can easily evaluate the derivatives of $\psi(r)$ and $\phi(r)$ for these potential models.

The values of γ computed from (6) for the Börn, Börn-Mayer, Lennard-Jones and the modified Varshni-Shukla potentials, hereafter referred to as γ_1 , γ_2 , γ_3 and γ_4 respectively, are presented in table 2 along with the experimental values.

The δ values have been obtained from (7) by substituting the experimental values of interionic distance r , γ , and the derivatives of $\phi(r)$ using the Börn model. This value of δ is represented by δ_1 . Similarly, the values of δ for Börn-Mayer, Lennard-Jones (12 : 6) and the modified Varshni-Shukla models hereafter referred to as δ_2 , δ_3 and δ_4 respectively, are shown in table 3 along with their indirect observed values.

3. Results and discussion

The computed values of the potential parameters A and n of the Börn potential, B and ρ of the Börn-Mayer model, λ of the Lennard Jones (12 : 6) potential and b and σ of the modified Varshni-Shukla potential are also given in table 1. It is seen

Table 1. Values of potential parameters

Crystal	Börn model		Börn-Mayer model		Lennard-Jones (12 : 6) model	Modified Varshni-Shukla model	
	A ($\text{erg} \times \text{cm}^n$)	n	B (10^{-12} erg)	ρ (\AA)	λ (10^{-106} erg \times cm^{12})	σ (10^{-12} erg)	b (10^{12} erg \times $\text{cm}^{-8/3}$)
LiF	6901.11×10^{-65}	6.457	2166.93	0.312	15146.76	251.825	1.506
LiCl	1329.95×10^{-77}	8.199	3636.58	0.313	187099.73	355.289	1.327
LiBr	6083.98×10^{-85}	9.323	11192.50	0.295	355716.99	946.705	1.198
LiI	8482.62×10^{-95}	10.538	37737.10	0.285	857215.94	1814.738	1.352
NaF	1114.76×10^{-66}	6.994	1090.07	0.331	66682.92	295.035	1.322
NaCl	1449.23×10^{-79}	8.495	4890.74	0.332	500281.69	569.415	1.196
NaBr	5329.62×10^{-79}	8.444	6935.44	0.338	928256.05	663.856	1.141
NaI	3551.53×10^{-89}	9.832	18627.60	0.329	2071098.20	1099.658	1.126
KF	6412.27×10^{-72}	7.733	2283.81	0.346	315831.41	409.851	1.179
KCl	1036.83×10^{-82}	8.962	7800.94	0.351	1691676.40	705.214	1.070
KBr	8857.75×10^{-83}	8.993	8049.78	0.367	2854268.00	692.376	1.001
KI	4716.46×10^{-88}	9.730	16817.90	0.363	5725221.80	993.687	0.977
RbF	1262.76×10^{-75}	7.979	2918.43	0.353	547975.84	451.979	1.126
RbCl	6798.60×10^{-83}	9.010	8183.70	0.365	2879267.20	724.401	1.006
RbBr	1678.31×10^{-83}	9.113	9067.93	0.378	4742468.90	738.026	0.950
RbI	3452.18×10^{-89}	9.770	17507.80	0.375	9064379.40	1020.341	0.926
CsCl	2821.26×10^{-114}	13.246	565972.00	0.270	5388885.30	8574.658	1.309
CsBr	2812.41×10^{-114}	13.278	584259.00	0.280	8706979.00	8664.727	1.234
CsI	2510.43×10^{-126}	14.947	3100580.00	0.265	15433735.00	22336.991	1.266

Table 2. Values of Grüneisen parameter γ

Crystal	γ (Exptl ^a)	γ (Exptl ^b)	γ_1	γ_2	γ_3	γ_4
LiF	1.7611	1.63	1.74	1.29	2.51	0.96
LiCl	1.7853	1.81	2.07	1.63	2.58	1.37
LiBr	2.0282	1.94	2.28	1.86	2.63	1.61
LiI	2.2325	2.19	2.51	2.10	2.70	1.86
NaF	1.8059	1.51	1.84	1.40	2.53	1.11
NaCl	1.7454	1.61	2.12	1.65	2.59	1.44
NaBr	1.7857	1.64	2.19	1.76	2.61	1.51
NaI	1.8967	1.71	2.38	1.95	2.66	1.72
KF	1.7398	1.52	1.99	1.53	2.57	1.25
KCl	1.6069	1.49	2.22	1.78	2.63	1.53
KBr	1.5841	1.50	2.23	1.79	2.63	1.53
KI	1.7262	1.53	2.37	1.94	2.67	1.69
RbF	1.4217	1.40	2.04	1.58	2.54	1.30
RbCl	1.5353	1.39	2.25	1.79	2.64	1.53
RbBr	1.5080	1.42	2.27	1.82	2.65	1.56
RbI	1.7430	1.56	2.40	1.95	2.67	1.70
CsCl	1.9700	—	3.05	2.64	2.91	2.42
CsBr	1.9300	—	3.07	2.67	2.92	2.43
CsI	2.000	—	3.37	3.53	3.05	2.75

^aSharma (1977); ^bSmith and Cain (1975)

from the table that, except for NaBr, the parameter A decreases from fluoride to iodide in each of the alkali halide series, whereas the parameter n increases in the same order. This indicates the volume dependence of the parameters A and n . Except for a few crystals (LiBr, LiI, NaI, KI, RbI, CsI) the potential parameters B , ρ , λ , and σ increase from lighter to heavier side of the alkali series. On the contrary, the parameter b decreases from lighter to heavier halides. We can therefore infer that the potential parameters evaluated in the present study are generally volume-dependent.

Table 2 also shows the calculated values of γ on the basis of equations (6) and (9), (6) and (10), (6) and (11) and (6) and (12). These are then compared with their observed values calculated from experimental data by Sharma (1977) and Smith and Cain (1975). It is interesting to note that all the computed values of γ obtained in the present work exhibit volume-dependence since the γ -values keep increasing from fluoride to iodide in each of the alkali series.

A critical study of table 2 shows that the γ -values obtained with the help of the modified Varshni-Shukla potential are better than other potential models. It is also observed that all the γ -values computed employing Lennard-Jones (12 : 6) potential are higher than the indirect observed values. This could be due to the fact that in this case $n=12$ has been taken for all the crystals in the present investigation, whereas actually n varies from crystal to crystal. We may, therefore, infer the order of superiority of these four potential models to study the γ -parameter as the modified Varshni-Shukla, Börn-Mayer, Börn and Lennard-Jones (12 : 6).

In table 3 the computed values of δ are compared with the indirect observed values obtained by Roberts and Ruppin (1971). It is observed that the δ values computed

Table 3. Values of Anderson-Grüneisen parameter δ

Crystal	δ (Exptl ^a)	δ_1	% dev	δ_2	% dev	δ_3	% dev	δ_4	% dev
LiF	—	4.72	—	3.93	—	5.73	—	3.45	—
LiCl	—	5.33	—	4.52	—	5.99	—	4.07	—
LiBr	—	5.73	—	4.93	—	6.17	—	4.49	—
LiI	—	6.18	—	5.38	—	6.40	—	4.94	—
NaF	3.75	4.91	+30.9	4.10	+9.30	5.80	+54.7	3.66	-2.4
NaCl	3.87	5.43	+40.0	4.56	+18.0	6.03	+55.8	4.18	+8.1
NaBr	4.13	5.56	+34.6	4.76	+14.5	6.09	+47.5	3.57	-13.6
NaI	4.16	5.92	+42.3	5.12	+24.0	6.27	+50.7	4.68	-12.5
KF	4.12	5.18	+25.7	4.34	+4.8	5.93	+43.9	3.87	-6.1
KCl	4.41	5.63	+27.7	4.81	+9.0	6.13	+39.0	4.34	-1.6
KBr	4.05	5.65	+39.5	4.82	+19.7	6.14	+51.6	4.35	+7.4
KI	3.98	5.92	+48.7	5.10	+30.1	6.27	+57.5	4.64	+16.6
RbF	5.05	5.27	+4.4	4.43	-11.8	5.97	+18.2	3.95	-21.8
RbCl	5.02	5.67	+12.9	4.83	-3.9	6.16	+22.7	4.35	-19.7
RbBr	4.81	5.71	+18.7	4.87	+1.2	6.11	+27.0	4.39	-19.8
RbI	4.53	5.96	+31.6	5.12	+13.0	6.30	+39.1	4.65	+2.6
CsCl	—	7.23	—	6.44	—	7.10	—	6.01	—
CsBr	—	7.27	—	6.00	—	7.14	—	6.04	—
CsI	—	7.86	—	7.07	—	7.64	—	6.65	—
Average Abs. %dev			29.75		13.29		42.3		11.0

^aRoberts and Ruppin (1971)

on the basis of Börn-model (δ_1) and Lennard-Jones model (δ_6) are higher and deviate appreciably from the experimental values for all the crystals. However the values δ_2 and δ_4 determined with the help of Börn-Mayer and the modified Varshni-Shukla potentials agree with their experimental values. It is also seen that for the twelve halides of sodium, potassium and rubidium the minimum and maximum percentage deviations in the δ_4 -values are -1.6 (KCl) and -21.8 (RbF). The average absolute percentage deviation of the computed values as compared with the experimental values are also shown in table 3. The minimum and maximum absolute percentage deviations in δ_4 and δ_3 values are 11.0 and 42.3 respectively. Thus the modified Varshni-Shukla potential model is superior to the Börn-Mayer followed by the Börn and the Lennard-Jones (12 : 6) potential models in calculating the δ -parameter using equation (5).

It is also noted from table 3 that δ_1 , δ_2 , δ_3 and δ_4 values of the alkali halide crystals generally show a volume-dependence except CsBr in Börn-Mayer; RbBr in Lennard-Jones and NaBr in modified Varshni-Shukla potential model.

To understand the behaviour of δ towards γ , graphs have been plotted and the least-squares method had been used to yield the best fitted equation of form

$$\delta = a_0 + a_1 \gamma + a_2 \gamma^2$$

where a_0 , a_1 and a_2 are the arbitrary constants.

For a group of four halides of a particular alkali metal, a pair of (δ , γ) value gives a set (a_0 , a_1 , a_2) value. Since four pairs of (δ , γ) values have been taken to study the variation of δ with γ , four sets of (a_0 , a_1 , a_2) values are obtained which are given in

Table 4. Values of constants a_0 , a_1 , a_2

Crystal	a_0	a_1	a_2
Lithium	2.91	0.52	0.31
	1.49	1.93	-0.04
	2.87	-0.57	0.69
	0.73	3.25	-0.55
Sodium	2.84	0.58	0.30
	2.92	0.16	0.50
	3.63	0.80	0.05
	0.11	4.34	-1.00
Potassium	1.12	2.23	-0.10
	-0.24	3.71	-0.49
	4.73	-0.13	0.25
	2.11	1.26	0.13
Rubidium	0.07	4.23	-0.50
	1.87	0.12	1.43
	4.80	-0.15	0.25
	-32.25	15.27	5.71
Caesium	0.61	-2.72	-0.11
	-0.02	3.45	-0.41
	0.00	2.38	0.03
	0.02	3.06	-0.24

table 4. In any row, the set of (a_0, a_1, a_2) values relates to pair (δ_n, γ_n) , where n denotes the number of the row. Thus for any group of halides in the first row ($n=1$), the set of (a_0, a_1, a_2) values correspond to (δ_1, γ_1) . Similarly in the second row, the set of values corresponds to (δ_2, γ_2) respectively and so on.

Chang (1967) showed a linear relation between δ and γ and obtained an equation of the form $\delta=2\gamma$. On comparing the present relation with Chang's expression we see that the latter is a particular case of the former where $a_0=a_2=0$ and $a_1=2$.

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