

## SIMPLE PROPERTIES OF CRYSTALS AND RESTSTRAHLEN FREQUENCY

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**ABSTRACT.** Born-Mayer lattice theory has been used to compute the simple bulk properties of alkali halides. For determining the constants of the potential function the Reststrahlen frequency instead of compressibility or molecular data has been used. Properties which have been computed are: cohesive energy, compressibility, thermal expansion, Grüneisen constant and elastic constants. In all cases the success according to the proposed procedure is either of the same order or is better than that obtained by the conventional procedures.

### INTRODUCTION

Born-Mayer theory (1932) has been widely applied and is now fairly well established for discussing the various bulk properties of ionic crystals. The general approach is to assume an analytical form for the interatomic potential function and then exploit the two familiar Born-Mayer conditions (1932) to evaluate the potential parameters. So far, in such approaches, information regarding thermal expansion  $\alpha$ , compressibility  $\beta$ , pressure and temperature derivatives of  $\beta$  are used. In the simplified approach based on this method often only  $\beta$  is used. The purpose of this article is to suggest the use of Reststrahlen frequency in its place. Once the potential energy function is thus completely determined, various bulk properties can be computed according to known procedures. Adopting this procedure we have computed the different properties of the alkali halide crystals. The properties discussed and compared with the experimental predictions are the cohesive energy  $W$ , compressibility  $\beta$ , thermal expansion  $\alpha$ , Grüneisen constant  $\gamma$ , and the different elastic constants. We consider also the simple Born-Mayer potential in which only the coulomb and overlap terms are considered. The reasons for choosing this simplified potential are many. Firstly, the contribution of all of the other types of forces to interaction potential is small and the effect on the calculation of most of the above mentioned properties is invariably negligible. Secondly, the comparison of the properties so computed with the values obtained when compressibility data are used instead of Reststrahlen frequency  $\omega_0$ , is possible in a straightway manner. The former type of calculations has been reported earlier by the authors (1964). Thirdly, this investment of computational labour is worth for the underlying idea is to illustrate the replacement of  $\beta$  by  $\omega_0$  even in a sophisticated calculation without any danger of impairing the accuracy.

## INTERATOMIC POTENTIAL

The simplified Born-Mayer potential (1932) which is used in this article is

$$\phi(r) = -\frac{\alpha e^2}{r} + A \exp(-r/\rho). \quad \dots (1)$$

Here  $\phi(r)$  is the interaction energy per atom,  $\alpha$  the Madlung constant,  $e$  the electronic charge,  $r$  the interatomic distance,  $A$  and  $\rho$  the two potential parameters which in the conventional procedure are determined from the Born-Mayer conditions (1932):

$$\left[ \frac{d\phi(r)}{dr} \right]_{r=r_0} = 0, \quad \dots (2)$$

and

$$\left[ \frac{d^2\phi(r)}{dr^2} \right]_{r=r_0} = \frac{9v_a}{\beta r_0^3}. \quad \dots (3)$$

Here  $v_a$  is the volume of the unit cell,  $r_0$  the equilibrium interatomic distance.

Kellermann (1940), and Sharan and Triwari (1964) have deduced expressions for  $\omega_0$  for NaCl and CsCl-type structures respectively on the assumption that the overlap extends only up to the nearest neighbours. The two relations can be conveniently combined into a single expression viz.,

$$\omega_0^2 = \frac{e^2}{\mu v_a} \left[ \frac{M}{6} (B' + 2A') - \frac{4\pi}{3} \right]. \quad \dots (4)$$

Here  $\mu$  is the reduced mass appropriate to the two kinds of ions in the crystal,  $M$  the coordination number, and  $A'$  and  $B'$  are defined as follows:

$$A' = \frac{2v_a}{e^2 r_0} \left[ \frac{dv(r)}{dr} \right]_{r=r_0} = -\frac{2\alpha v_a}{M r_0^3}, \quad \dots (5)$$

and

$$B' = \frac{2v_a}{e^2} \left[ \frac{d^2v(r)}{dr^2} \right]_{r=r_0} = \frac{2v_a}{M e^2} \left[ \frac{9v_a}{\beta r_0^3} + \frac{2\alpha e^2}{r_0^3} \right]. \quad \dots (6)$$

Here

$$v(r) = \frac{1}{M} A \exp(-r/\rho). \quad \dots (7)$$

Substitution of  $A'$  and  $B'$  from Eqs. (5) and (6) respectively in Eq. (4) leads to the following relation for  $\beta$ :

$$\beta = \frac{9v_a}{[3\mu v_a \omega_0^2 + 4\pi e^2] r_0^3} \quad \dots (8)$$

When  $\beta$  from Eq (8) is substituted in Eq (3) one obtains,

$$\left[ \frac{d^2\phi(r)}{dr^2} \right]_{r=r_0} = 3\mu\omega_0^2 + 4\pi \frac{e^2}{v_a} . \quad \dots (9)$$

In the present work we suggest to evaluate the constants  $A$  and  $\rho$  of Eq (1) from Eqs. (2) and (9). We shall refer this as the "proposed procedure" and the one in which use is made of Eqs. (2) and (3) as the "conventional procedure". The present endeavour aims at examining how far a single characteristic frequency is capable of explaining crystal properties. The two parameters  $A$  and  $\rho$  of Eq (1) can thus be calculated from the following explicit expressions obtained by applying conditions given by Eqs. (2) and (9) to Eq. (1) .

$$A = \frac{\alpha\rho e^2}{r_0^2} \exp(-r_0/\rho), \quad \dots (10)$$

and

$$\rho = \frac{\alpha e^2}{3\mu r_0^2 \omega_0^2 + \frac{2r_0^2 e^2}{v_a} \left( 2\pi + \frac{\alpha v_a}{r_0^3} \right)} . \quad \dots (11)$$

In this calculation the experimental values of  $\omega_0$  and  $r_0$  are needed.  $\omega_0$  values used here are those recorded in Table I, column 2, while  $\gamma_0$  values are those compiled by us earlier (1963). Thus, having determined the potential completely we proceed to calculate the various properties.

#### COHESIVE ENERGY

Cohesive energy per mole,  $W$ , is rather simply related with  $\phi(r_0)$  such that

$$W = -[N\phi(r_0) + c_0]. \quad \dots (12)$$

Here  $N$  is the Avogadro number and  $c_0$  the zero-point energy per mole. Values  $c_0$  have also been compiled by us (1963) earlier. Inserting Eq (1) into Eq (12) leads to the following working relation for  $W$  in terms of  $A$  and  $\rho$  .

$$W = - \left[ N \left\{ - \frac{\alpha e^2}{r_0} + A \exp(-r_0/\rho) \right\} + c_0 \right] . \quad \dots (13)$$

Computed values of the cohesive energy according to Eqs (10), (11) and (13) are recorded in Table I, column 4.

Experimental values are shown in column 3 of this very Table. The agreement is satisfactory. The average absolute deviation is 3.3 percent. According to the conventional procedure used by us (1964) earlier, the average absolute deviation is 2.9. This should be regarded as the first encouraging confirmation for the use of  $\omega_0$  data as an alternative to  $\beta$  suggesting by it the

validity of single frequency model for purposes of computing cohesive energy. A more crucial check is presented in the next section by calculating compressibility itself from  $\omega_0$

TABLE I  
Calculated and experimental values of  $W$ ,  $\beta$ ,  $\alpha$  and  $\gamma$ .

Crystal	$\omega_0$ ( $10^{12}\text{S}^{-1}$ )	$W$ (K Cal/mole)		$\beta(10^{-12}\text{dyne}^{-1}\text{cm}^2)$		$\alpha(10^{-6}\text{deg}^{-1})$		$\gamma$	
		Exptl (b)	Calcd.	Exptl (b)	Calcd.	Exptl (c)	Calcd.	Exptl (d)	Calcd.
	(a)								
LiF	5.73	242.2	245.3	1.43	1.39	34.0	27.9	1.99	1.48
LiCl	3.84	201.5	193.0	3.17	3.60	44.0	42.2	1.51	1.50
LiBr	3.26	191.5	180.2	3.90	4.78	50.0	45.3	..	1.49
LiI	2.71	180.0	164.7	5.30	6.93	59.0	61.0	..	1.76
NaF	4.63	215.4	220.7	2.06	1.83	36.0	31.7	1.57	1.79
NaCl	3.09	184.7	182.2	3.97	3.87	40.0	41.1	1.43	1.83
NaBr	2.54	175.9	172.3	4.75	4.81	43.0	44.5	1.55	1.86
NaI	2.20	166.3	159.5	6.21	6.47	48.3	50.0	1.59	1.88
KF	3.62	190.9	193.3	3.14	3.02	36.7	38.2	1.48	1.88
KCl	2.71	167.8	160.5	5.50	4.94	38.3	45.0	1.34	2.12
KBr	2.18	161.2	159.0	6.45	5.77	40.0	49.1	1.43	2.11
KI	1.94	152.8	149.4	8.07	7.21	45.0	52.1	1.58	2.25
RbF	3.01	185.0	182.8	3.66	5.04	33.33	42.6	1.28	1.85
RbCl	2.24	163.6	159.4	6.16	5.73	36.0	46.9	1.25	2.16
RbBr	1.69	158.0	153.3	7.38	6.55	38.0	49.9	1.27	2.23
RbI	1.41	149.7	142.5	9.00	8.25	43.0	41.0	1.50	1.77
CsF	2.39	176.6	170.0	4.25	3.92	....	..	1.49	1.75
CsCl	1.86	157.8	149.8	5.55	5.50	56.0	45.8	1.97	2.26
CsBr	1.39	152.3	144.6	6.28	6.06	..	..	1.93	2.43
CsI	1.17	145.4	136.6	7.83	7.35	....	....	2.00	2.53

(a) Compiled by Martin, D. H., 1965, *Advances in Phys.*, **14**, 30.

(b) Compiled by Kachhava, C. M. and Saxena, S. C., 1964, *Indian J. Phys.*, **38**, 388.

(c) Compiled by Kachhava, C. M. and Saxena, S. C., 1965, *Indian J. Phys.*, **39**, 145.

(d) Compiled by Born, M. and Huang, K., 1956, *Dynamical Theory of Crystal Lattices*, Clarendon Press, Oxford, 85

#### COMPRESSIBILITY

Compressibility,  $\beta$ , is related with Reststrahlen frequency,  $\omega_0$ , through the relation of Eq. (8). We employ this relation to compute  $\beta$  from the known values of the other quantities involved. The values so obtained are reproduced in column 6 of Table I in which are also listed in column 5 the experimental  $\beta$  values for a direct comparison. It is encouraging to note that the agreement between

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the experimental and calculated values is quite satisfactory. The average absolute deviation is 10.4 percent. It is interesting to compare this figure with 15.4 obtained in an earlier effort by us (1964) when molecular data and the relation of Eq. (2) were used to determine the potential parameters. This comparison in fact suggests a relative preference for the procedure suggested in this paper and thereby emphasizes the importance of the Reststrahlen frequency and its capability to predict the various crystal properties.

THERMAL EXPANSION

We have (1965a, 1966) recently derived an expression for the coefficient of thermal expansion,  $\alpha$ , in terms of the derivatives of  $\phi(r)$  and other quantities. For the sake of brevity only the final result is quoted here. It is

$$\alpha = - \frac{C_v}{2Nr_0} \frac{\phi'''(r_0)}{[\phi''(r_0)]^2}, \quad \dots (14)$$

in which  $C_v$  is the specific heat per mole at constant volume,  $\phi'''(r_0)$  and  $\phi''(r_0)$  are the third and second derivatives of  $\phi(r)$  at  $r = r_0$ , respectively. Equation (14) has been derived by Kumar (1959) adopting a different approach. For the form has been derived by Kumar (1959) adopting a different approach. For the form of Eq. (1) this gets simplified to the following expression.

$$\alpha = \frac{r_0 C_v}{2N\alpha e^2} \left( \frac{r_0^2}{\rho^2} - 6 \right) \left( \frac{r_0}{\rho} - 2 \right)^2. \quad \dots (15)$$

The values of  $\alpha$  are then readily calculated from Eq. (15) as all the other quantities are known and these  $\alpha$  values are recorded in column 8 of Table I, while the experimental values are given in column 7. In the earlier calculation of  $\alpha$  by us, (1966) based on Eq. (14) but where  $\beta$  was used to determine the unknown parameters of  $\phi(r)$  almost similar agreement between theory and experiment was achieved in spite of the fact that the dispersion terms in  $\phi(r)$  were also considered.  $C_v$  values used in the present calculations are the same as compiled in that paper (1966). The average absolute deviations in the present and previous calculations from the experimental data are 13.4 and 14.3 percent respectively. This is again an evidence for the suitability of the proposed method of fixing the interaction potential.

GRÜNEISEN CONSTANT

Recently we (1965a) have suggested a method for computing Gruneisen constant,  $\gamma$ , based on a single frequency model. Again we do not reproduce here the details of the derivation but quote only the final result which is,

$$\gamma = - \frac{r_0}{6} \frac{\phi'''(r_0)}{\phi''(r_0)}. \quad \dots (16)$$

For the form of  $\phi(r)$  of Eq. (1), Eq. (7) reduces to

$$\gamma = \frac{1}{6} \frac{\begin{pmatrix} r_0^2 \\ \rho^2 \end{pmatrix}}{\begin{pmatrix} r_0 \\ \rho \end{pmatrix} - 6} \quad \dots \quad (17)$$

In the calculation of  $\gamma$  therefore only  $\rho$  and  $r_0$  values are required. When  $\rho$  values obtained from Eq. (11) are employed we get the values of  $\gamma$  recorded in Table I, column 10. The agreement between theory and experiment is not very satisfactory and is also somewhat inferior to that obtained earlier by the authors (1965a). The reason for this lies partly in the use of a simplified potential (the dispersion terms have been neglected) which will affect the computation of  $\gamma$  and  $\alpha$  more than the other properties such as  $\beta$ ,  $W$ , etc. As our idea is more to demonstrate the success of the outlined procedure rather than computing the various properties accurately, we refrain from repeating calculations of  $\alpha$  and  $\gamma$  on a more detailed sophisticated potential.

#### ELASTIC CONSTANTS

The elastic constants can also be computed from the knowledge of the interatomic potential, Kachhava and Saxena (1965b). These calculations are confined to the Kellermann (1940), and Krishnan and Roy (1952) models. Parameters were determined either using the compressibility or molecular data. We reproduce here in brief only the important aspects of the calculation.

Thus, for NaCl-type crystals on the Kellermann potential (1940),

$$\phi(r) = -\frac{uv}{r} + 6v(r), \quad (18)$$

the elastic constant  $C_{11}$  is given by

$$C_{11} = \left[ -2.56 + \frac{B'}{2} \right] \frac{e^2}{2r_0^4},$$

where  $B'$  is defined by Eq. (6) and is given by

$$B' = \frac{2\mu\omega_0^2 r_0^3}{\rho} - 6.5169. \quad \dots \quad (19)$$

According to Sharan and Tiwari (1964) the three elastic constants for the CsCl-type crystals on the Kellermann model are given by the following expressions

$$C_{11} = \frac{9e^2}{32r_0^4} \left[ 5.621 + \frac{2}{3} (B' + 2A') \right], \quad \dots \quad (20)$$

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$$C_{12} = \frac{9e^2}{32r_0^4} \left[ -5.518 + \frac{2}{3} (B' - 2A') \right], \quad \dots (21)$$

and

$$C_{44} = \frac{9e^2}{32r_0^4} \left[ -2.815 + \frac{2}{3} (B' - 2A') \right], \quad \dots (22)$$

in which again the defining relations for  $A'$  and  $B'$  are the same as given by Eqs (5) and (6) respectively. These lead to finally

$$\left. \begin{aligned} A' &= -\frac{2\alpha}{3}, \\ B' &= \frac{2\mu\omega_0^3 r_0^3}{\sqrt{3}e^2} + 4.4985 \end{aligned} \right\} \dots (23)$$

TABLE II

The calculated and experimental values of  $C_{11}$  in units of  $10^{11}$  dyne  $\text{cm}^{-2}$

Crystal	Exptl.	Calcd	
		Kellermann model	Krusman and Roy model
LiF	11.35 (a)	11.74	11.82
LiCl	4.94 (a)	4.61	4.64
LiBr	3.94 (a)	3.45	5.64
LiI	2.85 (a)	2.37	2.35
NaF	9.71 (a)	10.55	10.83
NaCl	4.93 (a)	5.19	5.21
NaBr	4.02 (a)	4.22	4.23
NaI	3.035 (a)	3.16	3.17
KF	6.58 (a)	6.77	6.93
KCl	4.08 (a)	4.48	4.49
KBr	3.49 (a)	3.60	3.71
KI	2.775 (a)	3.16	3.17
RbF	5.7 (a)	5.35	5.37
RbCl	3.645 (a)	3.90	3.91
RbBr	3.185 (a)	3.43	3.44
RbI	2.585 (a)	2.74	2.75
CsF	. . . .	3.62	3.63
CsCl	3.64 (b)	4.05	4.10
CsBr	3.10 (b)	3.55	3.57
CsI	2.45 (b)	2.74	2.90

(a) Spangenberg, K. and Haussühl, S., 1957, *Z. Krist.*, **109**, 422.

(b) Haussühl, S., 1960, *Acta Cryst.*, **13**, 687.

The computed values of  $C_{11}$  on the Kellermann model for all the alkali halides are listed in Table II column 3 alongwith the experimental values in column 2. The average absolute deviation is 8.5%. This figure compares well with the one of 8.2 obtained when compressibility data are used in place of  $\omega_0$ .

In Table III, column 3, are shown the computed values of  $C_{12}$  obtained from the use of Eq (21) together with the experimental data in column 2. The average absolute percentage deviation is 18.1 which is a marked improvement over the figure of 25.1 corresponding to the use of  $\beta$ , i.e., the conventional procedure.

The values of  $C_{44}$  for the three CsCl-type crystals obtained according to Eq. (22) are recorded in Table III, column 6, along with the experimental data in column 5. Here the average absolute deviation of theory from experiment is only 7.6 per cent compared to 14.7 obtained from the use of  $\beta$ .

TABLE III

Calculated and experimental values of elastic constants in units of  $10^{11}$  dyne  $\text{cm}^{-2}$

Crystal	$C_{12}$			$C_{44}$		
	Exptl (a)	Calcd		Exptl (a)	Calcd.	
		Kellermann model	Krishnan and Roy model		Kellermann model	Krishnan and Roy model
CsCl	0.92	0.69	0.71	0.80	0.690	0.71
CsBr	0.84	0.70	0.75	0.75	0.694	0.75
CsI	0.71	0.62	0.64	0.62	0.61	0.64

(a) Hausühl, S., 1960, *Acta Cryst.*, **13**, 687.

On the model of Krishnan and Roy (1952) for NaCl-type crystals the working Eqs. are

$$C_{11} = [2\alpha(1+\delta) - 6\chi] \frac{e^2}{12r_0^4}, \quad \dots \quad (24)$$

and

$$C_{12} = C_{44} = 3(\chi - \alpha) \frac{e^2}{12r_0^4}, \quad \dots \quad (25)$$

while for CsCl-type these are

$$C_{11} = [2\alpha'(1+\delta) - 18\chi'] \frac{e^2}{16r_0^4}, \quad \dots \quad (26)$$

and

$$C_{12} = C_{44} = [\alpha'(2\delta - 7) + 9\chi'] \frac{e^2}{16r_0^4}. \quad \dots \quad (27)$$



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Here  $\delta = r_0/\rho$ ,  $\alpha' = 1.018$ ,  $X = 3.14$  and  $X' = 1.08$ . The values of  $C_{11}$  using Eqs. (24) and (26) are shown in Table II, column 4. The average absolute percentage deviation is 10.8 compared to 8.5 for the conventional approach. The values of  $C_{12}$  and  $C_{44}$  obtained from Eq. (27) are reproduced in columns 4 and 6 of Table III. For  $C_{12}$  the average absolute percentage deviation is 14.5 which is to be compared with the figure of 23.3 found from the conventional procedure. Again for  $C_{44}$  the average absolute deviation is 4.7 only which indicates great improvement over the figure 12.7 obtained previously. Thus we infer that the elastic constants are in general better reproduced through the use of  $\omega_0$  compared to  $\beta$  data or in other words, the proposed procedure is better than the conventional procedure.

### CONCLUSIONS

We now sum up the results obtained on the computation of different bulk crystal properties obtained on the proposed and conventional procedures in particular reference to their success in reproducing the experimental data. The values of cohesive energy of alkali halides are reproduced with almost equal success. In compressibility the proposed method leads to appreciably better results than the conventional procedure. Thermal expansion coefficients are also better reproduced on the basis of proposed method than the conventional approach. The Grüneisen constants on the other hand are well reproduced by the conventional method in comparison to the proposed one. On the other hand, the elastic constants are better reproduced by the proposed than the conventional method. The only exception is  $C_{11}$  where the conventional approach commands a relative superiority over the proposed one.

Thus on the whole we find that the use of Reststrahlen frequency instead of  $\beta$  in determining the potential parameters and then in predicting the properties, is preferable. It leads to a happy conclusion viz the use of Reststrahlen frequency in interpreting the bulk behaviour of crystals as encompassed in the different properties considered in this paper. Incidentally, this work also brings to light a link between lattice vibrations and the fundamental simple crystal properties through interatomic forces and that too in a very simple way.

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