COHESIVE ENERGY, COMPRESSIBILITY AND THERMAL EXPANSION OF DIATOMIC CRYSTALS

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ABSTRACT. In this paper we suggest various methods of calculating cohesive energy, compressibility and thermal expansion of diatomic crystals, and apply them for the particular case of alkali halides. The procedure suggested by us recently for evaluating one parameter of the potential energy function by using the molecular constants is upheld and confirmed, as the results, thus obtained, favourably compare with those based on crystal constants only.

INTRODUCTION

If the interaction potential energy between atoms of a crystal lattice be known several macroscopic properties can be predicted. However, even to fix the two unknown parameters of the simplest potential energy expression one needs the knowledge of equilibrium interionic separation in the lattice r_0, the compressibility β, its temperature and pressure derivatives, and the coefficient of thermal expansion α, Born and Huang (1956). Usually such data are not available and therefore alternative procedures which may not require the knowledge of so many crystal properties will be useful. A somewhat limited success only has been achieved in this direction by assigning a finite size to the ions or atoms constituting the lattice, Kettel (1956), Pauling (1960), and Kachhava and Saxena (1963a).

Recently we (1963b) have suggested to fix one of the parameters of the potential energy function of the diatomic crystals by considering the equilibrium internuclear separation and the force constant. This procedure therefore requires the knowledge of a comparatively smaller number of crystal properties and hence can be used for their determination. We in this paper propose to investigate in particular the diatomic alkali halide crystals and will consider the three simple properties viz., cohesive energy (W), β and α.

POTENTIALS AND DETERMINATION OF PARAMETERS

We will consider in our calculations the following three forms for the mutual potential energy per ion-pair in a crystal lattice, $\phi(r)$, :

$$\phi(r) = -\frac{\alpha e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + \frac{A_1}{r^n}, \qquad \ldots (1)$$

$$\phi(r) = -\frac{\alpha e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + A_2 e^{-r/\rho}, \qquad \ldots (2)$$

and

$$\phi(r) = -\frac{\alpha e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + A_3 e^{-\sigma r^2}. \qquad \ldots (3)$$

Here $\phi(r)$ is the potential energy of an ion-pair interacting with the rest of the lattice and with each other, r is the interionic separation, α the Madelung constant, C and D are the van der Waals constants, A_1, A_2, A_3, n, ρ and σ are the potential parameters. The first two are the familiar Born and Born-Mayer potentials respectively, while the third one is usually referred as the Gaussian potential and is due to Varshni and Shukla (1961). It will be noted that all the three potentials differ only in assuming the different forms for the overlap energy, and this form will be used to characterise the potential. The constants C and D have already been evaluated by Mayer (1933) and we have used the values given by him.

One constant of each potential i.e. n, ρ or σ can be determined using the molecular constants and adopting the procedure given by Kachhava and Saxena (1963*b*) except we have used potentials similar to those given by Eqs. (1) to (3). The other constant is evaluated from the condition,

$$\frac{\partial \phi(r)}{\partial r} = 0, \quad \text{at } r = r_0. \qquad \ldots (4)$$

A more general form of Eq. (4) is

$$r \frac{\partial \phi(r)}{\partial r} = \frac{3vT}{\beta}\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P. \qquad \ldots (5)$$

In Eq. (5) v is the volume of the molecule, V and P represent the volume and pressure respectively, and $\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P$ stands for α.

Born and Mayer (1932) have also derived the relation

$$r^2 \frac{d^2\phi(r)}{dr^2} = \frac{9v}{\beta}\left[1 + \frac{T}{\beta}\left\{\left(\frac{\partial \beta}{\partial T}\right)_P + \left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P\left(\frac{1}{\beta}\frac{\partial \beta}{\partial P}\right)_T\right\} + \frac{2}{3}T\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_P\right]. \qquad \ldots (6)$$

The quantity within square brackets in Eq. (6) is usually not much different from unity around room temperature and is equal to unity at absolute zero. Equation (6) is therefore very often used in the following simple form and specially when the various derivatives of β, and α are not known :

$$r^2 \frac{d^2\phi(r)}{dr^2} = \frac{9v}{\beta}. \qquad (7)$$

Equations (5) and (6) may be combined to eliminate α yielding the relation

$$r^2 \frac{d^2\phi(r)}{dr^2} = \frac{9v}{\beta}\left[1+\frac{T}{\beta}\left\{\left(\frac{\partial\beta}{\partial T}\right)_P + \frac{\beta r}{3vT}\left(\frac{\partial\phi(r)}{\partial r}\right)\left(\frac{1}{\beta}\frac{\partial\beta}{\partial P}\right)_T\right\} + \frac{2\beta r}{9v}\left(\frac{\partial\phi(r)}{\partial r}\right)\right]. \quad \ldots \quad (8)$$

Equation (8) can also be used to evaluate the second potential parameter if β and its temperature and pressure derivatives be known.

One can also eliminate β from Eqs. (5) and (7) so that

$$\frac{d\phi(r)}{dr} = \frac{\alpha r T}{3}\frac{d^2\phi(r)}{dr^2}. \quad \ldots \quad (9)$$

Equation (9) can also be used to determine the second potential parameter when α is known.

COHESIVE ENERGY

Thus, knowing the potential parameters, $\phi(r_0)$ and hence the cohesive energy per mole, W, is computed by the following relation :

$$W = -[N\phi(r_0)+\epsilon_0), \quad \ldots \quad (10)$$

Where N is the Avogadro's number and ϵ_0 is the zero-point energy per mole. We have used the ϵ_0 values given by Cubicciotti (1959).

Computed values of the cohesive energy for all the alkali halide crystals according to the various procedures outlined in the previous section are reported in Table I along with the experimental values. Columns 3, 5 and 7 list the calculated values according to the potentials of Eqs. (1), (2) and (3) respectively. The two potential parameters were determined in each case by using the molecular constants and the approximate condition given by Eq. (4). The agreement between theory and experiment is not satisfactory for the inverse potential but is good for the exponential and gaussian potentials with a preference for the former. To see the effect of using the approximate Eq. (4) we have also evaluated the potential parameters of the exponential potential in conjunction with the molecular constants and Eq. (5) and the values of cohesive energy so obtained are given in Col. 9 of Table 1. These values are in very much agreement with the values of Col. 5 thereby indicating that the use of Eq. (4) instead of Eq. (5) will not vitiate the values of W appreciably and is important, for Eq. (5) involves the knowledge of both α and β.

Evaluation of potential parameters from molecular constants and Eq.(9) yields values for W which are listed in Col. 11 of Table 1. These values refer to

the exponential potential and are also in good agreement with the experimental values. In an analogous fashion Eq. (8) can also be used instead of Eq. (9) to fix the second parameter of the potential energy function. The calculated values of cohesive energy obtained in this manner and on the exponential potential are reported in Col. 13 of Table 1. This approach, however, does not always lead to satisfactory results and in Table 1 we list only those cases where agreement with the experimental values is reasonable. The reason for the failure of this method can be easily understood if we look into the following expression used for the determination of the potential parameter A_2:

$$A_2 = \frac{\left(\frac{2\alpha e^2}{r_0} + \frac{42C}{r_0^6} + \frac{72D}{r_0^8}\right) + \frac{9v}{\beta}\left\{1 + T\left(\frac{1}{\beta}\frac{\partial\beta}{\partial T}\right)_P\right\} + \left\{\frac{3}{\beta}\left(\frac{1}{\beta}\frac{\partial\beta}{\partial P}\right)_T + 2\right\}\left\{\frac{\alpha e^2}{r_0} + \frac{6C}{r_0^6} + \frac{8D}{r_0^8}\right\}}{\frac{r_0}{\rho}\left[\frac{r_0}{\rho} + 2 + \frac{3}{\beta}\left(\frac{1}{\beta}\frac{\partial\beta}{\partial P}\right)_T\right]} \quad \ldots (11)$$

For all those substances where enhanced discrepancies are found it turns out that the value of A_2 is sensitively controlled by the terms containing $\frac{\partial\beta}{\partial P}$. It so happens that both numerator and denominator effectively become the difference of two almost equal quantities and as the accuracy with which $\frac{\partial\beta}{\partial P}$ is known is rather small we get absurd values for A_2 from Eq. (11).

We (1963c) have also recently computed the cohesive energies of all these compounds on these three potentials using the crystal properties only viz., Eqs. (5) and (6). The average absolute deviations for the inverse, exponential and gaussian potentials are 1.1, 0.97 and 0.95 per cent respectively. The results of Table 1 are thus of comparable accuracy and confirm the approach adopted in their calculation. This procedure has the advantage of unifying the molecular and crystal properties on the basis of one common parameter and also for determining the parameters, knowledge of α and β is not required and therefore these properties can be predicted. We will consider this possibility in the next two sections.

COMPRESSIBILITY

The potential determined from the knowledge of molecular constants and Eq. (4) can be used to calculate β from Eq. (7). This method is rigorous but for the fact that r_0 values used in computation refer to room temperature instead of 0°K. Actual calculations reveal that this approximation does not affect the

values of β very much and can be taken as an approximate method for evaluating it. Calculated values of β according to this procedure and for all the three potentials are given in Table 2. The direct experimental values at 25°C as well as those reduced to 0°A in conjunction with the data of Cubicciotti (1959) are also listed in this table for comparison. The values obtained on the basis of the inverse and gaussian potentials are inadequate while the exponential potential yields better results. The calculated values of β are also given for the exponential potential leaving van der Waals terms with a view to see the relative contributions of the latter. It will be noted that for better accuracy dispersion terms should be considered.

The two parameters of the potential energy function can also be determined by the use of molecular constants and the experimental value of the cohesive energy. This may, however,be not a very suitable approach as in ionic crystals the contribution of the overlap part to the total potential energy is only about 10%. Actual calculated values of β according to this procedure and Eq. (7) confirm this for the percentage deviations between theory and experiment usually increase as one considers the various halides of the same element from fluoride to iodide and also as the element is changed from Li to Cs.

Instead of using the molecular constants we can use Eq. (4) and the cohesive energy values to determine the two parameters of the potential energy function and then β is calculated from Eq. (7). Two sets of values of β obtained in this fashion, one for the exponential potential without dispersion terms and the other with dispersion terms, are given in Table II. The latter set of values are in better agreement with the experimental values and does exphasize the importance of dispersion terms in evaluating β. In these calculations of β we have made use of only the crystal properties and the fact that these are in good agreement with the values where molecular constants have been used to evaluate the common parameter, substantiates the latter approach.

We can also determine the potential completely by the knowledge of molecular constants and Eq. (9) and then β can be evaluated from Eq. (7). Values obtained in this way are also recorded in Table II and these are in good agreement with the experimental values at 25°C.

THERMAL EXPANSION

Theoretically speaking the two parameters of the potential can be determined using the molecular constants and either the cohesive energy or Eq. (8) and then α is calculated from Eq. (5). We could also employ the combination of cohesive energy and Eq. (8) and then in conjunction with Eq. (5) α can be calculated. In actual practice none of these methods yields satisfactory results the reason being the insensitivity of the cohesive energy for the purpose of evaluating the potential parameters and the small accuracy with which β and its derivatives are usually known.

TABLE I

Cohesive energy of alkali halide crystals in K cal/mole.

Substance	Exptl.	Inverse Potential c	%dev.	Exponential potential c	% dev.	Gaussian potential c	% dev.	Exponential potential d	% dev.	Exponential potential e	% dev.	Exponential potential f	% dev.
LiF	246.0*a*	240.3	−2.3	248.8	+1.1	262.7	+6.8	250.6	+1.9	250.7	+1.9	248.2	+0.8
LiCl	201.5*b*	189.0	−6.2	201.9	+0.2	210.3	+4.8	203.6	+1.0	203.9	+1.2	198.1	−1.5
LiBr	191.5*b*	176.9	−7.6	189.2	−1.2	197.3	+3.0	191.2	−0.2	191.3	−0.1	187.1	−2.3
LiI	180.0*b*	163.6	−9.1	174.6	−3.0	182.0	+1.1	176.9	−1.7	177.0	−1.7	172.1	−4.4
NaF	218.0*a*	—	—	—	—	—	—	—	—	—	—	—	—
NaCl	184.7*b*	176.6	−4.4	185.5	+0.4	190.0	+2.9	187.1	+1.3	189.2	+2.4	186.2	+0.8
NaBr	175.9*b*	167.9	−4.7	176.0	+0.1	181.8	+3.4	177.8	+1.1	179.0	+1.8	174.8	−0.6
NaI	166.3*b*	155.6	−6.4	163.3	−1.8	168.7	+1.4	165.1	−0.7	165.1	−0.7	165.7	−0.4
KF	193.0*b*	181.5	−6.0	193.8	+0.4	202.0	+4.7	195.4	+1.2	195.4	+1.2	194.5	+0.8
KCl	167.8*b*	161.7	−3.6	168.9	+0.7	174.1	+3.8	170.3	+1.5	170.4	+1.7	166.3	−0.9
KBr	161.2*b*	153.5	−4.8	159.6	−1.0	165.4	+2.6	162.2	+0.6	162.1	+0.6	164.4	+2.0
KI	152.8*b*	141.0	−7.7	149.2	−2.4	154.2	+0.9	151.1	−1.1	150.8	−1.3	—	—
RbF	—	180.0	—	189.7	—	195.9	—	191.1	—	191.3	—	—	—
RbCl	163.6*b*	155.3	−5.0	162.5	−0.7	167.6	+2.4	163.9	+0.2	163.9	+0.2	163.8	+0.1
RbBr	158.0*b*	149.2	−5.6	155.7	−1.5	159.0	+0.6	157.1	−0.6	157.2	−0.5	156.5	−1.0
BbI	149.7*b*	138.5	−7.5	145.1	−3.2	150.0	+0.2	146.8	−2.0	146.6	−2.1	141.2	−5.7
CsF	—	172.4	—	181.6	—	187.8	—	182.9	—	183.2	—	—	—
CsCl	157.8*b*	146.6	−7.1	154.5	−2.1	160.1	+1.5	156.7	−0.7	156.2	−1.0	—	—
CsBr	152.3*b*	139.5	−8.4	147.5	−3.2	153.2	+0.6	149.6	−1.8	149.5	−1.8	—	—
CsI	145.4*b*	122.8	−15.0	136.7	−6.0	142.2	+2.2	139.1	−4.3	138.4	−5.0	—	—
Avg. Abs. % dev.			6.6		1.7		2.5		1.3		1.5		1.6

a. Plendl, J. N., 1961, *Phys Rev.*, **123**, 1174.
b. Born, M., and Huang, K., 1956, Dynamical Theory of Crystal Lattices, (Oxford : Clarendon Press).
c. Potential parameters determined using the molecular constants and Eq. (4).
d. Potential parameters determined using the molecular constants and Eq. (5).
e. Potential parameters determined using the molecular constants and Eq. (9).
f. Potential parameters determined using the molecular constants and Eq. (8).

TABLE II

Compressibility (β) of alkali halide crystals in 10^{-12} cm^2 dyne^{-1}

Substance	Exptl. 298°A	Exptl. 0°A	Inverse Potential d	% Dev.	Simple* Exponential Potential d	% Dev.	Exponential potential d	% dev.	Gaussian potential d	% dev.
LiF	1.43a	1.34	1.90	+41.8	1.28	−4.5	1.26	− 6.0	0.71	−47.0
LiCl	3.17a	3.04	3.53	+16.1	2.61	−14.1	2.49	−18.1	1.54	−50.0
LiBr	3.90a	3.44	4.59	+33.4	3.56	+ 3.6	3.20	− 7.0	1.97	−42.7
LiI	5.30a	4.52	6.16	+35.8	4.67	+ 3.1	4.32	− 4.4	2.68	−40.7
NaF	2.06a	1.94	—	—	—	—	—	—	—	—
NaCl	3.97a	3.24	4.42	+36.4	3.58	+10.5	3.42	+ 5.5	2.32	−28.4
NaBr	4.75a	4.17	5.32	+27.6	4.37	+10.0	3.79	− 9.1	2.80	−32.9
NaI	6.21a	5.29	7.17	+35.5	5.94	+13.0	5.52	+ 4.3	3.75	−29.1
KF	3.14a	2.95	4.25	+44.1	3.25	+10.2	3.07	+ 4.1	1.93	−34.6
KCl	5.50a	4.93	5.96	+20.9	5.00	+ 1.4	4.68	− 6.1	3.25	−10.2
KBr	6.45a	5.53	7.54	+36.4	6.36	+15.0	5.96	+ 7.8	4.14	−24.8
KI	8.07a	7.25	10.11	+39.4	8.91	−23.0	8.28	+15.0	5.74	−20.8
RbF	3.66a	3.44	3.81	+10.8	3.05	−11.3	2.83	−17.7	1.84	−46.5
RbCl	6.16a	5.61	7.01	+25.0	5.91	+ 5.3	5.45	− 2.7	3.76	−33.0
RbBr	7.38a	6.14	8.10	+31.9	6.98	+13.7	6.41	+14.3	5.07	−17.4
RbI	9.00a	7.98	11.35	+42.2	9.86	+23.7	9.01	+13.0	6.25	−21.7
CsF	4.25a	4.00	4.34	+ 8.5	3.32	−17.0	3.02	−24.5	2.00	−50.0
CsCl	5.55a	4.64	6.77	+46.0	5.62	−21.1	4.91	+ 5.8	3.20	−31.0
CsBr	6.28a	5.61	7.63	+36.0	7.20	+28.4	5.75	+ 2.5	3.85	−31.4
CsI	7.83a	6.62	12.98	+96.4	10.80	+63.1	9.48	+43.2	6.04	− 8.8
Avg.	Obs.	% dev.		35.4		15.4		10.9		31.6

TABLE II—(*contd.*)

Substance	Exptl. 298°A	Exptl. 0°A	Simple* Exponential potential	% dev.	Exponential potential *e*	% dev.	Exponential potential *f*	% dev.	Exponential potential *g*	% dev.
LiF	1.43*a*	1.34	1.52	+13.4	1.39	+ 3.7	1.14	−14.9	1.34	− 6.3
LiCl	3.17*a*	3.04	2.67	−13.9	2.53	−16.8	2.45	−19.4	2.77	−12.6
LiBr	3.90*a*	3.44	2.88	−16.3	2.83	−17.7	3.66	− 6.3	3.63	− 6.9
LiI	5.30*a*	4.52	2.91	−35.6	3.08	−39.1	6.30	+39.4	5.02	− 5.3
NaF	2.06*a*	1.94	2.18	+12.4	2.13	+ 9.8	—	—	—	—
NaCl	3.97*a*	3.24	3.63	+12.0	3.58	+10.5	3.27	+ 1.0	4.35	+ 9.6
NaBr	4.75*a*	4.17	3.69	−11.5	4.16	0.0	5.68	+36.2	4.60	− 3.2
NaI	6.21*a*	5.29	4.16	−21.4	6.93	+31.0	4.16	−21.4	6.27	+ 1.0
KF	3.14*a*	2.95	3.24	+10.2	3.19	− 8.1	2.95	0.0	3.34	+ 6.4
KCl	5.50*a*	4.93	4.79	− 2.8	5.03	− 2.0	4.36	−11.5	5.12	− 6.9
KBr	6.45*a*	5.53	5.31	− 3.8	5.74	+ 3.8	6.20	−12.1	6.62	+ 2.6
KI	8.07*a*	7.25	5.61	−22.6	6.42	−11.4	10.94	+50.9	8.31	+ 3.0
RbF	3.66*a*	3.44	—	—	—	—	—	—	3.12	−12.0
RbCl	6.16*a*	5.61	4.41	−21.4	5.05	−10.0	5.90	+ 5.2	6.02	− 2.3
RbBr	7.38*a*	6.14	4.44	−27.6	5.51	−10.3	7.51	+22.3	7.11	− 3.7
RbI	9.00*a*	7.98	4.79	−40.0	6.40	−19.8	13.31	+66.8	10.08	+12.0
CsF	4.25*b*	4.00	—	—	—	—	—	—	3.37	−20.7
CsCl	5.55*c*	4.64	2.22	−52.2	3.86	−16.8	6.37	+37.3	5.67	+ 2.2
CsBr	6.28*c*	5.61	2.22	−60.5	4.13	−26.4	8.29	+47.8	6.60	+ 5.1
CsI	7.83*c*	6.62	1.47	−77.8	4.80	−27.5	24.62	+272.0	10.80	+37.8
Avg.	abs.	% dev.		25.2		14.3		—		8.2

a. Spangenberg, K., 1956, Naturewissenschaften, **43**, 394; Spangenberg, K., and Haussuhl, S., 1957, *Z. Krist.*, **109**, 422.
b. Huggings, M. L., 1937, *J. Chem. Phys.*, **5**, 143; 1947, *Ibid.*: **15**, 212.
c. Bridgmann, P., 1940, *Proc. Amer. Acad. Arts. Sci.*, **74**, 21.
d. Potential parameters evaluated using molecular constants and Eq. (4) and β calculated from Eq. (7).
e. Potential parameters evaluated using cohesive energy and Eq. (4) and β calculated from Eq. (7).
f. Potential parameters evaluated using molecular constants and cohesive energy.
g. Potential parameters evaluated using molecular constants and Eq. (9).
*Exponential potential without dispersion terms.

TABLE III

Thermal expension (α) of alkali halide crystals in $10^{-5}/°C$.

Substance	Exptl. *a*	Exponential potential	
		b	*c*
LiF	9.2	17.9	—
LiCl	12.2	36.4	14.10
LiBr	14.0	23.1	− 8.72
LiI	16.7	22.8	27.83
NaF	9.8	—	—
NaCl	11.0	16.5	−60.25
NaBr	11.9	15.5	7.34
NaI	13.5	12.3	− 5.96
KF	10.0	13.8	− 0.965
KCl	10.1	16.8	4.76
KBr	11.0	8.1	6.11
KI	12.5	7.9	16.48
RbF	9.5	45.7	—
RbCl	9.85	13.3	10.22
RbBr	10.4	14.3	8.42
RbI	11.9	−0.13	17.03
CsF	9.5	33.3	—
CsCl	13.65	11.5	17.23
CsBr	13.9	8.7	20.57
CsI	14.6	−18.7	22.64

a. Huggings, M. L., 1937, J. Chem. Phys., **5**, 143.

b. Potential parameters evaluated using molecular constants and Eq. (7) and then α is calculated from Eq. (5).

c. Potential parameters evaluated using molecular constant and cohesive energy and then α is calculated from Eq. (5).

However, for the approximate estimation of α we found two methods fairly satisfactory and dependable. The two parameters can be determined with the use of Eq. (7) and either the molecular constants or the cohesive energy and subsequently α is calculated from Eq. (5). Computed values of α according to both these procedures for the exponential potential are given in Table 3 along with the experimental values. The agreement between theory and experiment is only approximate and is obvious because of the use of Eq. (7) which is not rigorous. Nevertheless, these methods can be used with reliance for estimating the values of α. The listings of Table III further confirm the approach of evaluating the common parameter of the potential from the use of molecular constants instead of crystal constants.

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