Properties of Ionic crystals on Born-Mayer theory

By C. M. Kachhava

Physics Department, University of Rajasthan, Jaipur, India

AND

S. C. Saxena

Department of Energy Engineering, University of Illinois, Chicago, U.S.A.

(*Received* 24 *May* 1967—*Revised* 12 *November* 1969

This paper considers a number of crystal properties around room temperature in the spirit of Born-Mayer lattice theory. Specifically, the properties calculated are : thermal expansion, Gruneisen constant, reststrahlen frequency, dielectric and elastic constants. The potential, used explicitly includes the three types of interactions between the positive and negative ions, present in the lattice. A comparison of the results is made with the experimental data as well as with another from of interaction potential, which may be treated as a simplified form of the present one. The results are reasonably satisfactory in view of the employment of approximate theories.

INTRODUCTION

One of the most complete forms for the effective interaction potential per ion pair is :

$$\Phi(r) = -\frac{\alpha e^2}{r} - \frac{C}{r^6} - \frac{D}{r^8} + Mbc + -e^{(r_+ + r_- - r)/\rho}$$

$$+ M'\frac{b}{2}\left[c_{--}e^{(2r_- - ar)/\rho} + c_{++}e^{(2r_+ - ar)/\rho}\right] \qquad .. (1)$$

The various symbols have meanings as given in the papers of Born & Mayer (1932) and Huggins & Mayer (1933). In the evaluation of the potential parameter ρ, use has been made of the Born-Mayer thermodynamical condition. The choice of b is completely arbitrary and it has the value 10^{-12} erg per molecule. These authors exposed the above potential to test by calculating interionic distances, cohesive energy, compressibility and characteristic frequency. The computations were later on repeated by Cubicciotti (1959) using the newly available data. He was successful in achieving a certain amount of improvement in the results.

However, the arbitrariness in the choice of ionic radii and potential parameter gave ample scope for Fumi & Tosi (1964) and Tosi & Fumi (1964) to further improve the results. They adopted a very elaborate procedure to compute the values of b, ρ and the ionic radii. These authors have confined themselves to the calculations of only cohesive energy of alkali

alides   The present work endeavours to extend the ideology of Fumi and Tosi for the calculations of other crystal properties.

CALCULATION OF PROPERTIES.

One of the thermodynamical relations due to Born and Mayer (1932) is

$$\beta = 9vF_{T,P}r_0^{-2}\left[\frac{d^2\phi(r)}{dr^2}\right]_{r=r_0}^{-1} \qquad ...(2)$$

with

$$F_{T,P} = 1 + \frac{T}{\beta}\left(\frac{\partial\beta}{\partial T}\right) + \frac{T}{\beta^2 V}\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial\beta}{\partial P}\right)_T + \frac{2T}{3V}\left(\frac{\partial V}{\partial T}\right)_P \qquad .. (3)$$

Huggins (1937) and Cubicciotti (1959) have calculated β for the two cases. In one case $F_{T,P} = 1$, while in the other it is not so. These lead to crude estimates only. We do not expect any appreciable improvement by employing the newly determined parameters As such the calculations are not proposed to be repeated.

Kachhava & Saxena (1966a) have shown that the coefficient of thermal expansion is expressed reasonably well by the relation,

$$\alpha = -C_v\phi'''(r_0)[\phi''(r_0)]^{-2}(2r_0N)^{-1}. \qquad ...(4)$$

Here C_v is the molar specific heat at constant volume and the primes indicate the order of differentiation with respect to interatomic distance. The results are displayed in table 1.

Gruneisen constant γ is another property for which accurate experimental data are available   A simple approach for its theoretical estimation was advanced by Kachhava & Saxena (1966a), according to which

$$\gamma = -r_0[6\phi''(r_0)]^{-1}\phi'''(r_0). \qquad ...(5)$$

Table 1 also lists the theoretical values of γ obtained from equation (5) on the basis of the potential of equation (1).

The characteristic reststrahlen frequency ω_0 of an ionic crystal is also related to $\phi(r)$, as is evident from the work of Kellermann (1940), and Krishnan & Roy (1952). For NaCl-type crystals, we have

$$\omega_0^2 = \left[(B + 2A) - \frac{4\pi}{3}\right](\mu v)^{-1}e^2, \qquad ...(6)$$

in which μ is the reduced mass and

and $A = e^{-2}r_0^{-1}v\,v'(r_0),$

$B = 2e^{-2}v\,v''(r_0).$

Here $Mv(r)$ is the contribution of overlap to $\phi(r)$, where M is the coordination number. Computed values of the frequencies according to

4

equation (6) in conjunction with equation (1) are cited in table 1 along with the experimental values.

An alternative procedure has been adopted by Huggins (1937). It can be best summarized by quoting the general expression for the force constant k applicable to all classes of structures given by Born & Huang (1956). It is

$$k = \frac{M}{3}\left[v''(r_0) + \frac{2v'(r_0)}{r_0} \right] \qquad (7)$$

The values of ω_0 computed through the relation,

$$\omega_0{}^2 = \mu^{-1} k \qquad ...(8)$$

are recorded in the last column of table 1.

TABLE 1. COMPARISON OF EXPERIMENTAL AND VARIOUS CALCULATED
VALUES OF α, γ and ω_0

Crystal	$\alpha(10^{-6}/^0C)$		γ		$\omega_0(10^{12} s^{-1})$		
	Exptl [a]	Cal. Eqn. (1)	Exptl.[b]	Cal. Eqn. (1)	Exptl.[c]	Cal. Eqn. (6)	Eqn. (8)
LiF	34.0	37.1	1.64	1.37	5.73	...	10 3
LiCl	44.0	62.2	1.69	1.84	3.84	2.76	4.40
LiBr	50.0	56.5	1.88	1.99	3.26	3.81	5.24
LiI	59.0	60.1	2.03	1.67	2.71	2.74	4.12
NaF	36.0	57.8	1.83	1.64	4.63	2.99	5.16
NaCl	40.0	35.4	1.64	1.88	3.09	3.33	4 17
NaBr	43.0	53.2	1.72	1.91	2.54	2.57	2.96
NaI	48.3	65.8	1.66	1.91	2.20	1.99	2.72
KF	36.7	47.3	1.58	1.74	3.62	3.15	4.09
KCl	38.3	50.0	1.49	1.83	2.71	2.69	3.21
KBr	40.0	54.9	1.46	2.05	2.18	2.29	2.67
KI	45.0	62.8	1.45	2.11 −	1.94	1.93	2.20
RbF	31.67	47.7	1.37	1.95	3.01	3.64	3.70
RbCl	36.0	52.5	1.57	2.14	2.24	2.51	2.80
RbBr	38 0	43.7	1.43	1.81	1.69	1.80	2.04
RbI	43.0	61.5	1.51	2.30	1.41	1.57	1.72
CsF	...	...	1.49	2.35	2.39	3.66	3.80

a. Kachhava C. M. & Saxena S. C. 1965 *Indian J. Phys.* **39**, 145.

b. Kachhava C. M. 1966 *Ph. D. Thesis : Certain Problems of Solid State Physics*, Rajasthan University,

c. Kachhava C. M. & Saxena S. C. 1966 *Indian J. Phys.* **40**, 567.

The appropriateness of the two theories is to be judged on the basis of the fact that both neglect the electronic polarizablities of the ions. Further, the relative assessment of the two must be made by keeping in view the inclusion and exclusion of the Lorentz field correction effect associated with ionic displacements in equations (6)and (8), respectively.

The classical theory of dielectric constant (Mott & Gurney 1948) and its relationship with interaction potential is elaborated by Kachhava & Saxena (1966b). Here we quote only the final result which connects ϵ_0 (the low frequency dielectric constant) with the high frequency constant $\epsilon \propto$ the effective charge s and δ. The relation and defining equations are

$$\frac{\epsilon_0 - 1}{3 + (\epsilon_0 - 1)s} = \frac{\epsilon\propto - 1}{3 + (\epsilon\propto - 1)s} + \frac{(4/3)\pi\, \delta}{1 - (4/3)\pi\,\delta\,(1 - s)}, \qquad \ldots(9)$$

$$\delta = Ne^2\, k^{-1} \quad \text{and} \quad s = 1 + e^{-2r_0^2 v'(r_0)}$$

Employing the observed values of $\epsilon\propto$ as given by Born & Huang (1956), we have calculated ϵ_0 and these results are contained in table 2.

TABLE 2. THE EXPERIMENTAL AND VARIOUS CALCULATED VALUES OF ϵ_0 AND THOSE OF C_{11}, C_{12} AND C_{44} IN UNITS OF 10^{11} erg/cm³

Crystal	ϵ_0		C_{11}		Exptl. [b]		Cal. $C_{12} = C_{44}$
	Exptl.[a]	Eqn. (9)	Exptl.[b]	Cal	C_{12}	C_{44}	
LiF	8.96	...	11.35	7.17	4.80	6.35	5.27
LiCl	11.95	...	4.94	3.28	2.26	2.49	3.05
LiBr	13.25	...	3.94	4.02	1.88	1.91	2.52
LiI	16.85	..	2.85	2.40	1.40	1.35	1.96
NaF	5.10	58.9	9.71	6.04	2.43	2.80	3.66
NaCl	5.91	9.51	4.93	5.76	1.31	1.275	1.67
NaBr	6.38	11.3	4.02	4.23	1.15	0.99	1.41
NaI	7 26	19.5	3.035	2.62	0.90	0.72	1.14
KF	5.46	18.9	6.58	5.42	1.49	1.28	2.23
KCl	4.87	7.74	4.08	4.34	0.69	0.635	0.98
KBr	4.91	7.37	3.49	4.14	0.58	0.51	0.80
KI	5.10	8.81	2.775	3.12	0.47	0.38	0.64
RbF	6.48	11.3	5.7	6.11	1.25	0.91	1.86
RbCl	4.92	1.34	3.645	4.65	0.61	0.475	0.78
RbBr	4.87	6.55	3.185	3.79	0.48	0.385	0.65
RbI	4.94	6.99	2.585	3.30	0.375	0.281	0.51
CsF	.		...	7 09	...	.	1.53

a. Martin D. H. 1965 *Advances in Phys.* 14, 39.
b. Spangenberg K. & Haussuhl S. 1957 *Z. Krist.* 109, 422.

Lastly, we consider the elastic constants. The general expressions for the elastic constants have been given by Cowley (1962) and they depend on the crystal structure. Thus, for the NaCl-type crystals,

$$C_{11} = \frac{e^2}{vr_0}\left[\frac{1}{2}(A + A' + A'' + B' + B'') - 2.55604\right] \quad (10)$$

and

$$C_{12} = C_{44} = \frac{e^2}{vr_0}\left[\frac{1}{4}(A' + A'' - B' - B'') + 0.6955\right] \quad ...(11)$$

in which

$$A = \frac{2v}{e^2}\ v_{12}''\ (r_0),\quad B = \frac{2v}{e^2r_0}\ v_{12}'\ (r_0),\quad A' = \frac{2v}{e^2}\ v_{11}'\ 2^{1/2}(r_0)$$

$$B' = \frac{2^{1/2}}{e^2r_0}\ v_{11}'2^{1/2}\ (r_0),\quad A'' = \frac{2v}{e^2}\ v_{22}''\ 2^{1/2}(r_0)$$

$$\text{and } B'' = \cdots\cdots \quad \frac{2^{1/2}v}{e^2r_0}\ v_{22}'\ 2^{1/2}\ (r_0).$$

$$\left.\rule{0pt}{60pt}\right\} \quad (12)$$

The application of these equations to the potential of equation (1) is straightforward. Calculated values of C_{11}, C_{12} and C_{44} are to be found in table 2 together with experimental data.

DISCUSSION

We now critically examine the different calculated properties reported in tables 1 and 2 with reference to corresponding experimental data. The reproduction of α is in general not very satisfactory. The calculated values of γ exhibit the same trend as α, in accordance with our expectation.

It may be noted that the method based on equation (8) leads to values which are always greater than those obtained on the basis of equation (6). The relative superiority of the simple equation (6) can be gauged from the fact that it yields theoretical values which agree within the average absolute deviation of 10.5% only in contrast to 30.5% for equation (8).

The method suggested here for the calculation of dielectric constant is rather discouraging. In particular, the values for lithium halides are negative. This failure is to be ascribed to the crude nature of the dielectric theory employed, rather than to the form of the interaction potential given by equation (1). It is therefore desirable to employ more advanced formulations of dielectric theories such as of Szigeti (1949, 50) and of Dick & Overhauser (1958). We have worked on these theories and the results are published elsewhere.

The reproduction of elastic constants from equation (11), though not excellent, may be reasonably well. Indeed any simpler theory of this type is not likely to succeed satisfactorily for the description of elastic constants, for it has to predict the non-equivalence of C_{12} and C_{44} and then explain the difference quantitatively. It may be pointed out that this inequality in the elastic constants results from the assumption of non-central forces (Cowley 1962). Woods *et al* (1960), and Cowley *et al* (1963) have achieved good success by adopting such an approach for NaI and KBr. Considerable success has also been achieved by Dick (1963) to explain the difference between C_{12} and C_{44} by the shell model due to Dick & Overhauser (1958).

References

Born M. & Huang K. 1956 *Dynamical Theory of Crystal Lattices*, Clarendon Press, Oxford.
Born M. & Mayer J. E. 1932 *Z. Physik* 75, 1.
Cowley R. A. 1962 *Proc. Roy. Soc (London)* A268, 121.
Cowley R. A. Cochran W. Biockhouse B. N. & Woods A D. B. 1963 *Phys. Rev.* 131, 1030.
Cubicciotti D. 1959 *J. Chem Phys.* 31, 1646.
Dick B. G. 1963 *Phys. Rev.* 129, 1583.
Dick B. G. & Overhauser A. W. 1958 *Phys. Rev.* 112, 90.
Fumi F. G. & Tosi M. P. 1964 *J. Phys. Chem. Solids* 25, 31.
Huggins M. L 1937 *J. Chem. Phys.* 5, 143.
Huggins M. L. & Mayer J. E. 1933 *J. Chem. Phys.* 1, 643.
Kachhava C. M. & Saxena S. C. 1966a *Indian J. Phys.* 40, 273.
                                    1966b *Indian J. Phys.* 40, 225.
Kellermann E. W. 1940 *Phil. Trans. Roy. Soc.* 238, 513.
Krishnan K S. & Roy S. K. 1952 *Proc. Roy. Soc.* A210, 481.
Mott N. F. & Gurney R. W. 1948 *Electronic Processes in Ionic Crystals*, Clarendon Press, Oxford.
Sangeti B 1949 *Trans. Faraday Soc.* 45, 155.
Szigeti B. 1950 *Proc. Roy. Soc.* A204, 51.
Tosi M. P. & Fumi F. G. 1964 *J. Phys. Chem. Solids* 25, 45
Woods A. D. B., Cochran W. & Blockhouse B. N. 1960 *Phys. Rev.* 119, 980.