COHESIVE ENERGIES AND OTHER PROPERTIES OF IONIC CRYSTALS

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Many properties of gases and liquids have been calculated and explained in terms of a commonly used interaction energy function, such as Lennard-Jones (12:6) potential. In an ionic crystal, the charge distribution on each ion has approximately spherical symmetry and they interact according to central force law. Thus, it seems reasonable to assume that ions of an ionic crystal are of the same electronic structure as an inert gas, possess overlap energy (and Van der Waals energy), following a law with the same interionic distance variation as for two inert gas atoms. It is therefore, possible to describe a number of properties of ionic crystals on a common basis with the help of Lennard- Jones (12:6) potential in conjunction with the term for Coulomb energy. This, thus, affords a unified approach for evaluating and interpreting the properties of ionic crystals as well as the knowledge about the interaction forces and it is reasonable to assume that such an analysis will achieve considerable success.

The energy per cell in an ionic crystal may be represented as

$$\phi(r) = \left(- \frac{\alpha e^2}{r} + \frac{B}{r^{12}} - \frac{C}{r^6} + \epsilon_0 \right) \qquad \ldots (1)$$

where α is Madelung's constant, e is the electronic charge, r is the interionic distance, B is the repulsive parameter which is calculable, C is the Van der Waals constant and ϵ_0 is zero point vibrational energy.

In Eq. (1) we have not considered the dipole-quadrupole Van der Waals term and effect of overlap potentials other than the nearest neighbours because they do not alter the estimates of various properties appreciably.

Finding the first and second derivaties of Eq. (1) and equating it with the well known expressions involving compressibility, molar volume and temperature (Huggins, 1937) expresions for the parameters B and C can be derived and their values obtained with the help of the experimental data for various observable properties. Alternatively, B can be obtained in the above manner and C can be used directly from the optical data of Huggins and Mayer (1933).

TABLE I

| Crystal | Cohesive energy in K Cal/mole | | | | | Compressibility in 10^{12} cm²/dyne | | Coefficient of thermal expansion × 10^6 | | |
	Experimental	Calculated (present work)	Calculated (Fowler)	Calculated (Cubicciotti)[a]	Calculated (Huggins)[a]	Experimental[a]	Calculated (present work)	Experimental	Calculated (present work)	Calculated (Born model)[b]
CsF	—	182.4	176.9	179.2	175.7	4.25 (4.25)	3.97	—	—	—
CsCl	157.8	156.8	157.3	155.9	153.1	5.95 (5.55)	5.53	56.0	55.27	56.18
CsBr	152.3	151.6	153.5	151.1	149.6	7.06 (6.28)	6.39	—	—	—
CsI	145.4 (141.5)H	142.9	147.7	143.6	142.5	8.57 (7.83)	7.44	—	—	—
RbCl	163.6	167.0	165.7	164.3	162.0	6.65 (6.16)	5.45	36.0	31.52	41.05
RbBr	158.0	162.6	160.6	157.6	156.1	7.94 (7.38)	6.60	38.0	42.61	41.90
RbI	149.7	150.1	153.5	149.1	148.0	9.57 (9.06)	8.57	—	—	—
KBr	161.2	165.5	166.3	162.7	161.3	6.70 (6.45)	5.45	40.0	37.44	43.08
KI	152.8	155.1	158.8	153.4	152.4	8.54 (8.07)	7.13	—	—	—
NaI	166.3	166.8	170.8	165.9	164.3	7.07 (6.21)	4.68	48.3	47.99	42.87

(H) Huggins (1937)
(a) Cubicciotti (1959)
(b) Kumar (1960)

pressions can be derived for various crystal properties and the values of the B and C can be used to compute them. Following this scheme we calculated the values of the cohesive energy, compressibility and the coefficient of linear expansion for a few representative alkali halide crystals (reported in Table 1,) and compared them with the experimental values and also with other determinations. The results based on the Lennard-Jones (12:6) potential are quite consistent with other determinations. The discrepancies with the experimental data become more pronounced as we proceed towards lighter alkali halides but the agreement is quite satisfactory for heavier compounds. Details and also computations for other metal halide crystals heavier than alkali halides will be published later.

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REFERENCES

Cubicciotti, D., 1959, *J. Chem. Phys.*, **31**, 1646.

Fowler, R.H., 1955, 'Statistical Mechanics' (Oxford University Press).

Huggins, M.L., 1937, *J. Chem. Phys.*, **5**, 143.

Huggins, M.L., and Mayer, J.E., 1933, *J. Chem. Phys.*, **1**, 643.

Kumar, S., 1959, *Proc. Nat. Inst. Sci. India*, **25**, 364.