

Letters to the Editor

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Lattice energy and thermal expansion of diatomic crystals

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In the present work we have computed the cohesive energy and the coefficient of volume expansion of the alkali halide crystals by considering the modified $V-S$ type of repulsion interaction term of the form $\lambda \exp(-\mu r^{3/2})$. Considering the above interaction term in conjunction with the electrostatic, the dipole-dipole and the dipole-quadrupole interaction energy terms, the crystal energy per mole may be expressed as

$$W = -[N\psi(r_0) + \epsilon_0] \quad \dots (1)$$

where N is the Avogadro's Number, $\psi(r_0)$ is the lattice energy per cell and ϵ_0 is the zero point energy per mole. The parameters λ and μ have been evaluated employing the Hildebrand's (1931) static lattice conditions. Computed values of the cohesive energy using equation (1) for a few ionic crystals are reported in table 1. The present theoretical values of W using equation (1) are in better agreement with the observed values than with those calculated by Kachhava & Saxena (1964) using the Gaussian model.

Following Smyth (1955), Kumar (1959) has developed a simple method to compute coefficient of volume expansion α_v . A general form of Kumar's equation can be expressed as

$$\alpha_v = - \frac{C_p}{2r_0} \frac{\psi'''(r_0)}{[\psi''(r_0)]^2} \sqrt{Z} \quad \dots (2)$$

in which r_0 is the interionic equilibrium separation distance, $\psi'''(r_0)$ and $\psi''(r_0)$ refer to the values of third and second derivatives of $\psi(r)$ at $r = r_0$ respectively, C_p the specific heat at constant pressure and $Z = (Z_c N_c + Z_a N_a) / (N_c + N_a)$ where Z_c , N_c and Z_a , N_a are the charge number of cation and anion, respectively. Substituting the values of $\psi'''(r_0)$ and $\psi''(r_0)$ for the modified $V-S$ model, equation (2) becomes

$$\alpha_v = - \frac{C_p \left[\frac{6\alpha e^2}{r_0^4} + \frac{336C}{r_0^9} + \frac{720D}{r_0^{11}} + \frac{K}{2} \left(\frac{9b}{2r_0^{3/2}} + \frac{1}{2r_0^3} - \frac{9b^2}{2} \right) \right]}{2r_0 \left[-\frac{2\alpha e^2}{r_0^3} - \frac{42C}{r_0^8} - \frac{72D}{r_0^{10}} - \frac{K}{2} \left(\frac{1}{r_0^2} - \frac{3b}{r_0^{\frac{5}{2}}} \right) \right]^2}, \quad \dots (3)$$

where
$$K = \left(\frac{\alpha e^2}{r_0} + \frac{6C}{r_0^6} + \frac{8D}{r_0^8} \right)$$

The theoretical values of α_v using equation (3) are reported in the table 1 along with the experimental values. It is seen from the table that the agreement between the experimental and calculated values is satisfactory and our values are better than the theoretical values of Kachhava & Saxena (1965) obtained by employing the same method but assuming different potential energy function. Thus the present approach demonstrates the necessity and importance of using the correct potential energy function in computing the lattice properties of ionic crystals.

TABLE 1. Cohesive energy and thermal expansion of alkali halide crystals

Crystal	Cohesive energy Kcal/mole			$\alpha_v \times 10^6$ per degree		
	Exptl.	Theoret eqn. (1)	Kachhava & Saxena (1964)	Exptl.	Theoret eqn. (3)	Kachhava & Saxena (1965)
LiCl	201.5	198.9	210.3	44.0	40.10	44.76
LiBr	191.5	187.1	197.3	50.0	40.67	44.68
NaCl	184.7	184.4	190.0	40.0	39.41	42.20
NaBr	175.9	175.0	181.8	43.0	43.22	46.45
KCl	167.8	167.6	174.1	38.3	43.58	47.29
KBr	161.2	160.6	165.4	40.0	47.33	51.05
RbCl	163.6	161.8	167.6	36.0	49.43	47.58
RbBr	158.0	154.7	159.0	38.0	47.78	51.61
CsCl	157.8	154.0	160.1	56.0	45.81	49.36
CsBr	152.3	148.5	153.2	—	—	—

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