

LATTICE ENERGIES AND OPTOELECTRONIC PROPERTIES OF SOME IONIC CRYSTALS

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Simple relations are proposed for the evaluation of lattice energies based on the assumption that linear relation between lattice energies and inter-ionic distances within a molecular group of halides. These relations are applied to some ionic crystals and to estimate lattice energies. Our results are in good agreement with experimental values in comparison with the results of Kapustiniskii and Kudriavstev's theories. A modified well-known Moss formula applicable to alkali halides is also presented. A new linear relation relating to energy gap and refractive index has also been proposed and evaluated the electronic polarizabilities. The average percentage deviation with our relation is only 5.6 per cent, whereas 10.9 per cent is the deviation in the work of Kumar *et al.*¹ Evaluated E_G and the electronic polarizabilities conclude that our work is an improvement over Kumar *et al.*

Key Words : Lattice Energies; Refractive Indices; Band Energy Gap; Electronic Polarizabilities, Alkali Halides

INTRODUCTION

THERE have been various theoretical methods²⁻⁴ starting with the Born-Mayer model to evaluate the lattice energy of the ionic crystals apart from the experimental method based on the Born-Haber cycle.⁵ All the methods enumerated in literature⁶ for the evaluation of lattice energies involve many experimentally determined parameters and tedious mathematical calculations. Hence, a simple and straight relation has been proposed to evaluate the lattice energies of alkali Ga, In, Tl and divalent halides and the results are presented in this paper.

Keeping the importance of electronic polarizability and energy gap in mind, Kumar *et al.*¹ presented a modification of the well-known Moss formula.⁷ The results obtained with Kumar *et al.*¹ method are not in good agreement with experimental values. As such, the present authors took up the present investigation and proposed a new relation relating the energy gap to the refractive index. The simplicity of the above relations are discussed and electronic polarizabilities are evaluated.

RELATIONS RELATING TO LATTICE ENERGIES, INTER IONIC DISTANCE AND ENERGY GAP, REFRACTIVE INDEX AND ELECTRONIC POLARIZABILITY

It is assumed that there is a linear relationship between lattice energies and inter-ionic distances within the molecular group halides. The following relations are obtained for various molecular group halides and are as follows :—

$$U = - 49.51 (r_0) + 324.72, \quad \dots(1)$$

(Alkali halides)

$$U = - 144.30 (r_0) + 901.00 \quad \dots(2)$$

(Divalent halides)

and
$$U = - 47.75 (r_0) + 286.54, \quad \dots(3)$$

(Ga, In, Tl halides)

where U and r_0 are the lattice energy (kcal/mol) and inter-ionic distance (Å). The constants in the above relations are unique in the sense that they represent the best fit with experimental data. The interionic distance (Å) related to the above work have been taken from Boswarva and Murthy⁸ and Carlin.⁹

The refractive index is related to the energy gap by the well-known Moss relation⁷ and is given by

$$E_G n^4 = 173, \quad \dots(4)$$

where E_G and n are energy gap and refractive index. Kumar *et al.*¹ have given the following modified equation

$$E_G n^4 = 52. \quad \dots(5)$$

In the present study, we propose a relation, which is similar to eq (5).

$$E_G n^4 = 44.8 \quad \dots(6)$$

It is assumed again that a linear relation between refractive index and energy gap within a molecular group halides. Based on this assumption, the equation given below is proposed, i.e.,

$$E_G = -9.12n + 22.18, \quad \dots(7)$$

where n and E_G are refractive index and energy gap (in eV). Experimental values of n are used to get E_G in equation (7). The obtained E_G values from equation (7) are used for the evaluation of electronic polarizabilities (α) of the alkali halides utilizing the below given equation.

$$\alpha = 0.396 \times 10^{-24} \left[\frac{\sqrt{44.8/E_G} - 1}{\sqrt{44.8/E_G} + 2} \right] \frac{M}{d} \quad \dots(8)$$

The symbols involved in the above equation have their usual significance and are similar to the equation of Kumar *et al.*¹ The experimental data presented by Kumar *et al.*¹ have been taken and employed in the above equations to solve for n , E_G and α .

RESULTS AND DISCUSSION

The relevant data from the literature^{1,8,9} have been used to evaluate the lattice energies of some ionic crystals. The evaluated lattice energies for alkali halides, divalent, Ga, In and Tl halides using eqs. (1) to (3) are presented in Tables I and II.

TABLE I

Evaluated values of lattice energies (k cal/mol), energy gaps (eV), refractive indices and electronic polarizabilities ($\times 10^{-24}\text{cm}^3$) for alkali halides.^a

Salt	<i>U</i>	<i>U</i>	<i>n</i>	<i>EG</i>	α	α
	Present study Eq. (1)	Ref. (9)	Present study Eq. (6)	Present study Eq. (7)	Present study Eq. (8)	Ref. (1)
LiF	225.9	245.6	1.390	9.5	1.095	1.032
LiCl	198.9	207.9	1.455	7.0	2.735	2.428
LiBr	190.4	196.9	1.515	5.9	3.661	3.269
LiI	178.6	171.6	1.660	4.4	6.414	6.010
NaF	211.1	227.7	1.437	10.0	1.764	1.885
NaCl	186.6	192.4	1.511	8.1	3.311	3.497
NaBr	178.4	181.6	1.553	7.2	4.224	4.422
NaI	166.5	169.6	1.667	6.0	5.926	6.463
KF	193.6	200.7	1.424	9.8	2.556	2.625
KCl	170.5	173.2	1.515	8.6	4.457	4.901
KBr	163.1	163.7	1.548	7.9	5.376	5.916
KI	151.9	156.7	1.639	6.8	7.155	8.133
RbF	186.6	191.9	1.441	9.4	3.281	3.393
RbCl	163.3	164.9	1.529	8.5	5.133	5.746
RbBr	155.9	156.5	1.553	8.0	6.108	6.795
RbI	145.1	148.6	1.553	7.2	7.902	9.244
CsF	175.9	182.8	1.455	8.6	4.358	4.372
CsCl	148.5	155.3	1.538	7.5	5.432	5.693
CsBr	140.9	149.3	1.563	6.9	6.435	6.458
CsI	129.1	138.6	1.633	5.9	8.434	8.768
Average percentage deviation :	1.38	2.13			5.58	10.91

^aFor the comparison of experimental and other values of *U*, *n*, *EG* and α , vide Refs 1, 6, 11, 12 and 15.

It is concluded from the keen observation of Tables I and II that linear relation between lattice energy and inter-ionic distance holds good in the case of all types of halides reported in the present study. It is observed that the lattice energies computed with eqs. (1) and (3) for alkali and Ga, In, Tl halides are in excellent agreement with the experimental values. The average percentage deviation between calculated and experimental values is also given for the alkali halides except LiF and CsI. Kapustinskii^{10,11} and Kudriavstev's¹² theories predict a rather significant difference of values compared to present values. Merits and demerits of Kapustinskii's work are clearly demonstrated by Waddington.³

The reason for the deviation of Kudriavstev's results from experimental and other theories is attributed to the simplified assumptions involved in the theory.¹³ In the case of divalent halides, lattice energies computed with eq. (2) predicts fairly good values and are comparable with the experimental values except for

Beryllium halides. The reason for the divergence in the case of Beryllium halides may be due to the lack of good experimental data on interionic distance and lattice energies. Our results in the case of divalent halides of CaF_2 , BaF_2 , SrF_2 and SrCl_2 are in good agreement with experimental values^{3,14} in comparison with the results of Kudriavstev's theory.²

TABLE II
Estimated lattice energies (k cal/mol) for divalent and Ga, In, Tl halides.^a

Crystal	Present study Eq. (2)	Carlin (Ref. 9)	Crystal	Present study Eq. (2)	Carlin (Ref. 9)
BeF_2	699	839	CaBr_2	516	514
BeCl_2	649	720	CrI_2	486	491
BeBr_2	625	692	SrF_2	584	592
BeI_2	698	665	SrCl_2	516	509
MgF_2	646	700	SrBr_2	494	488
MgCl_2	587	599	SrI_2	464	463
MgBr_2	564	575	BaF_2	566	557
MgI_2	538	547	BaCl_2	494	485
CaF_2	598	628	BaBr_2	470	466
CaCl_2	539	537	BaI_2	440	439
GaCl	181.3	—	InI	154.9	153.3
GaBr	174.1	—	TlF	186.9	195.0
GaI	163.5	—	TlCl	167.8	170.9
InCl	171.8	170.1	TlBr	161.4	166.6
InBr	165.0	161.8	TlI	161.6	162.1

^aFor the comparison of experimental and other values of lattice energies *vide* Refs. 3, 13, 14 and 16.

In the present study, the modification of the Moss relation applicable to alkali halides is also given by eq (6). To evaluate reliable E_G values based on the experimental refractive indices, eq. (7) is proposed. Employing eq. (7) with experimental (n) values, energy gaps are evaluated for alkali halides and the results are presented in Table I. These E_G values (obtained from eq. 7) are utilized and the electronic polarizabilities of alkali halides are estimated. The obtained electronic polarizabilities with the equation (8) are in good agreement with the experimental values. The average percentage deviation between calculated and experimental values is only 5.58 per cent in the present case, whereas, 10.9 per cent is the deviation in the work of Kumar *et al.*¹ Here, the percentage deviations in both cases are without fluorine molecules. The least average percentage deviation (5.58 per cent) indicated the soundness of our relation (eq. 8). It proves that the estimated E_G values are correct in magnitude. Evaluated E_G and electronic polarizabilities of alkali halides show that our work is an improvement over that of Kumar *et al.*¹

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