

## The Born repulsive parameters and dielectric behaviour of alkali halides

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**Abstract.** The dependence of the Born repulsive parameters of alkali halides on elastic and dielectric data has been discussed. The values of hardness parameter in alkali halides have been recalculated using the revised values of van der Waals energies. It is observed that the two sets of hardness parameter corresponding to elastic and dielectric data differ from each other but become compatible if an effective charge parameter for the ions is introduced. Its usefulness has been demonstrated by calculating the strain derivative of static dielectric constant of alkali halides.

**Keywords.** Alkali halides; Born repulsive parameters; effective charge parameter; strain derivative of static dielectric constant.

### 1. Introduction

It has recently been pointed out by Boswarva (1972) and Boswarva and Simpson (1973) that the Born-Mayer repulsive parameters derived from the experimental data on dielectric constants in alkali halides turn out to be significantly different from the corresponding values estimated from their compressibility or elastic data. We show in the present paper that this discrepancy can be eliminated if one introduces an effective charge parameter for the ions. The concept of effective charge parameter in the dielectric theory of alkali halides has been a subject of detailed investigations (Szigeti 1950, Dick and Overhauser 1958, Halon and Lawson 1959, Hardy 1960). First we calculate the repulsive hardness parameter  $\rho$  in alkali halides using revised values of van der Waals dipole-dipole and dipole-quadrupole energies and the more accurate data on dielectric constants (Lowndes and Martin 1969). The values of  $\rho$  thus calculated from dielectric data are found to be smaller than those obtained by using the compressibility data. This prediction is in accordance with Boswarva's earlier investigation. The two sets of hardness parameter corresponding to dielectric and elastic data become compatible if we introduce an effective charge parameter for the ions. Using the concept of effective charge parameter we calculate the strain derivative of static dielectric constant of alkali halides.

## 2. Calculation of repulsive hardness parameter

The short range repulsive potential in ionic crystals is represented by the exponential form of the type  $B \exp - (R/\rho)$  where  $R$  is the interionic separation and  $B$  and  $\rho$  are the Born repulsive parameters. The hardness parameter  $\rho$  can be calculated from the compressibility data in a conventional manner using the following equation (Tosi 1964):

$$\frac{R}{\rho} = \frac{\alpha_M \frac{e^2}{R} + \frac{6c}{R^6} + \frac{8d}{R^8} - \frac{3VT\beta}{K}}{\frac{9V}{K} + 2\alpha_M \frac{e^2}{R} + \frac{42c}{R^6} + 72 \frac{d}{R^8}} \quad (1)$$

where  $\alpha_M$  is the Madelung constant,  $\beta$  is the thermal expansion coefficient,  $K$  is the isothermal compressibility and  $V$  is the volume per ion pair. Values of van der Waals dipole-dipole coefficients  $c$  and dipole-quadrupole coefficients  $\alpha$  in alkali halides were calculated by Mayer (1933) using the polarizabilities of ions corresponding to free state. In fact the polarizabilities of ions in crystals (Tessman *et al* 1953) differ significantly from the free state polarizabilities reported by Pauling (1927). We have, therefore, revised the Mayer's values of  $c$  and  $d$  in alkali halides using the crystalline polarizabilities of ions derived by Pirenne and Kartheuser (1964) from the experimental refraction data. The excitation energy parameters used in the calculations of  $c$  and  $d$  were evaluated following a method recently proposed by Boswarva (1970). Values of  $c$  and  $d$  thus calculated have been listed in table 1. The magnitudes of  $c$  and  $d$  are found to be larger by a factor of 1.5 than the corresponding values reported by Mayer. The values of various input parameters appearing in eq. (1) have been taken from Tosi (1964). Values of  $\rho$  calculated from eq. (1) are reported in table 1.

An alternative method for evaluating  $\rho$  is that suggested by Boswarva (1972) who has, in fact, used the Clausius-Mossotti and Lorentz-Lorentz relations for static dielectric constant  $\epsilon_s$  and high frequency dielectric constant  $\epsilon_\infty$  respectively. Thus one can write

$$\frac{\epsilon_s - 1}{\epsilon_s + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3} \frac{\alpha_I}{V} \quad (2)$$

where  $\alpha_I$  is the polarizability arising from the relative displacements of ions. Following Mott and Littleton (1938) one can write

$$\alpha_I = \frac{Z^2 e^2}{A} \quad (3)$$

$$A = 2 \left[ \phi''(R) + \frac{2}{R} \phi'(R) \right] \quad (4)$$

and

$$\phi(R) = B \exp - \left( \frac{R}{\rho} \right) - \frac{c}{R^6} - \frac{d}{R^8} \quad (5)$$

$A$  is the force constant between nearest neighbours and  $\phi(R)$  is the short range potential,  $Ze$  is the charge on the ions. We have calculated the values of  $\rho$  from eq. (2) with the help of eqs (3) to (5) taking data on dielectric constant from

Table 1. Values of  $c$  (in  $10^{-60}$  erg cm<sup>6</sup>),  $d$  (in  $10^{-76}$  erg cm<sup>8</sup>),  $\rho$  (in Å) and  $Z'$ .

Crystal	$c$	$d$	$\rho$ Calculated from		$Z'$		
			Eq. (1)	Eq. (2)	(a)	(b)	(c)
LiF	23·42	18·18	0·29	0·23	0·86	0·81	0·88
LiCl	168·08	179·205	0·31	0·26	0·94	0·79	0·90
LiBr	269·25	336·563	0·33	0·28	0·92	0·73	0·90
LiI	493·31	756·03	0·40	..	..	..	0·88
NaF	102·22	85·37	0·31	0·23	0·83	0·83	0·86
NaCl	325·50	355·22	0·32	0·25	0·86	0·77	0·84
NaBr	461·64	651·77	0·33	0·23	0·85	0·74	0·82
NaI	740·10	1234·86	0·37	0·22	0·82	0·73	0·83
KF	258·29	286·13	0·32	0·28	0·92	0·91	0·87
KCL	689·71	1069·53	0·33	0·27	0·89	0·81	0·84
KBr	915·86	1570·07	0·31	0·26	0·91	0·78	0·84
KI	1331·11	2612·90	0·36	0·25	0·81	0·74	0·82
RbF	357·65	444·96	0·31	0·27	0·93	0·95	0·88
RbCl	931·89	1586·83	0·32	0·29	0·94	0·83	0·84
RbBr	1219·34	2281·03	0·34	0·28	0·89	0·80	0·83
RbI	1740·08	3692·89	0·35	0·27	0·85	0·74	0·85

(a) Calculated in the present study.

(b) From Lowndes and Martin (1969).

(c) From Dick and Overhauser (1958).

Lowndes and Martin (1969). The values of  $\rho$  thus obtained have also been listed in table 1.

### 3. Evaluation of the strain derivative of static dielectric constant

It is apparent from table 1 that the values of  $\rho$  calculated from the dielectric constants eq. (2) are consistently lower than the corresponding values calculated from the compressibility data eq. (1). This discrepancy, for the first time, was noticed by Mott and Littleton (1938) and was attributed by them to the deviation of the local Lorentz field from its nominal value  $(4\pi/3)\rho$ . However, it has been confirmed by several investigators (Pirenne and Kartheuser 1964, Theimer and Paul 1965) that the deviations from the value  $(4\pi/3)\rho$  of the Lorentz field due to ionic overlap in alkali halides are negligible.

It has been emphasised by numerous investigators (e.g., Lowndes and Martin 1969) that within the framework of the classical theory of dielectric constant, the experimental data can be accounted only if one assumes an effective charge  $Z'e$

on the ions. ( $Z'/Z$ ) is known as the effective charge parameter and its value is always less than 1. For alkali halides  $Z=1$  and therefore  $Z'/Z = Z'$ . Replacing  $Z$  by  $Z'$  in eq. (3) we have evaluated  $Z'$  such that the values of  $\rho$  derived from the compressibility data become compatible with the corresponding values obtained from the dielectric data. It is convincing to observe from table 1 that the values of  $Z'$  thus obtained are less than 1 in every crystal. For the sake of comparison we have included in table 1 the values of effective charge parameter  $Z'$  reported by Lowndes and Martin (1969) and by Dick and Overhauser (1958). Our values of  $Z'$  are closer to those obtained by Dick and Overhauser who employed an exchange charge polarization model. It is an interesting empirical observation which can be supported theoretically by the exchange charge polarization model based on the Lowdin's quantum mechanical theory of ionic overlap (1956). The inclusion of the exchange charge polarizations (Dick and Overhauser) modifies the expression for  $\alpha_i$  (eq. (3)) as follows

$$\alpha_i = \frac{Z^2(e+D)^2}{A} \quad (6)$$

where  $D$  is the exchange charge polarization parameter. In fact  $Z(e+D)$  is not identical with the effective charge parameter introduced by Szigeti as the latter also contains the contribution arising from the short range interaction polarization discussed at length by Dick and Overhauser. This is why our values of  $Z'$  show deviations from the values of Szigeti effective charge parameter reported by Lowndes and Martin (table 1).

Thus it is clear from the above discussion that there are two alternatives for describing the dielectric behaviour of ionic crystals with the help of Born-Mayer short range interaction model. The first alternative is that suggested by Boswarva in which one has to obtain an entirely different set of the Born repulsive parameters. The second alternative is that developed in the present paper in which a single set of repulsive parameters with the concept of effective charge is capable of explaining the elastic as well as the dielectric properties of ionic crystals. In order to make a more powerful test of these two alternatives we calculate the strain derivative of static dielectric constant ( $\partial\epsilon_s/\partial V$ ). The differentiation of eq. (2) with respect to  $V$  yields

$$\frac{3V}{(\epsilon_s+2)^2} \frac{\partial\epsilon_s}{\partial V} - \frac{3V}{(\epsilon_\infty+2)^2} \frac{\partial\epsilon_\infty}{\partial V} + \frac{\epsilon_s-1}{\epsilon_s+2} - \frac{\epsilon_\infty-1}{\epsilon_\infty+2} = \frac{4\pi}{3} \frac{\partial\alpha_i}{\partial V} \quad (7)$$

where

$$\frac{\partial\alpha_i}{\partial V} = -\frac{e^2}{A^2} \frac{\partial A}{\partial V}. \quad (8)$$

Equation (8) has been derived directly by differentiating eq. (3) with respect to  $V$ . We have estimated  $\partial\alpha_i/\partial V$  from eqs (4), (5) and (8) using the values of repulsive parameters obtained from the dielectric data. The values of  $(\partial\epsilon_s/\partial V)$  have then been calculated from eq. (7) taking  $(\partial\epsilon_\infty/\partial V)$  from Sharma *et al.* The values of  $V(\partial\epsilon_s/\partial V)$  for alkali halides thus obtained have been given in table 2.

Using the concept of effective charge a modified expression for  $(\partial\epsilon_s/\partial V)$  can be obtained which reads as under (Jones, 1967):

$$\frac{9V}{4\pi(\epsilon_s+2)^2} \frac{\partial\epsilon_s}{\partial V} + \frac{\epsilon_s-1}{\epsilon_s+2} \frac{3}{4\pi} = \frac{(e+D)}{A^2} \left[ 2A \frac{\partial D}{\partial V} - (e+D) \frac{\partial A}{\partial V} \right]. \quad (9)$$

**Table 2.** Values of  $D$  ( $10^{-10}$  e.s.u.),  $\partial D/\partial V$  ( $10^{12}$  e.s.u./cm<sup>3</sup>) and  $V(\partial\epsilon_s/\partial V)$  for alkali halides.

Crystal	$D$	$\partial D/\partial V$	$V(\partial\epsilon_s/\partial V)$				
			Calculated		Experimental		
			(a)	(b)	(c)	(d)	(e)
LiF	-0.29	4.27	34.95	30.78	29.41	22.95	30.89
LiCl	-0.28	2.24	53.08	37.01	..	30.36	..
LiBr	-0.58	4.03	65.09	40.84	..	40.32	..
NaF	-0.38	3.79	15.75	14.68	11.97	12.52	12.76
NaCl	-0.50	3.50	19.21	14.62	14.31	13.02	14.69
NaBr	-0.63	3.66	21.30	15.85	15.49	14.86	15.87
NaI	-0.62	2.76	26.52	18.25	18.11	16.55	..
KF	-0.21	1.51	16.70	13.38	..	12.74	..
KCl	-0.50	2.54	14.66	10.60	8.91	8.45	9.27
KBr	-0.62	2.90	15.23	10.77	8.61	8.35	9.03
KI	-0.75	2.91	16.21	10.59	8.91	8.16	..
RbF	-0.11	0.77	20.37	14.15	..	14.46	..
RbCl	-0.34	1.69	14.56	9.27	8.63	7.79	..
RbBr	-0.56	2.36	14.90	8.99	7.93	7.46	..
RbI	-0.82	3.04	15.27	8.90	6.83	6.94	..

(a) Calculated using the values of  $\rho$  from dielectric data.

(b) Calculated using the values of  $\rho$  from elastic data and concept of effective charge.

(c) From Jones (1967).

(d) From Lowndes and Martin (1969).

(e) From Fontanella *et al* (1972).

For evaluating  $A$  and  $\partial A/\partial V$  appearing in eq. (9) we have used repulsive parameters determined from compressibility data.  $D$  and  $\partial D/\partial V$  have been taken from Sharma *et al* and listed in table 2.  $V(\partial\epsilon_s/\partial V)$  for alkali halides calculated from eq. (9) have also been listed in table 2. For the sake of comparison we have included in table 2 the experimental values of  $V(\partial\epsilon_s/\partial V)$  compiled from recent studies (Jones 1967, Lowndes and Martin 1969, Fontanella *et al* 1972). It is informative to observe from table 2 that  $V(\partial\epsilon_s/\partial V)$  calculated from the concept of effective charge are very close to those observed experimentally. On the other hand  $V(\partial\epsilon_s/\partial V)$  calculated from the first alternative of Boswarva are significantly larger than the experimental values. Thus the concept of effective charge is not only physically plausible but also has the additional advantage of describing the elastic as well as the dielectric properties with a single set of repulsive parameters.

### Conclusion

It has been shown that the two sets of repulsive parameters obtained by Boswarva (1972) become compatible if we introduce an effective charge parameter for the ions in alkali halides. The concept of effective charge parameter, thus introduced, has been supported by previous investigations in the field of dielectric behaviour of alkali halides. Values of the strain derivative of static dielectric constant have been estimated on the basis of the exchange charge polarization model which are found to present a close agreement with experiment.

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