PATH-PD 70-0837

Schottky defects in alkali halides and compressibility

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MS. received 13*th October* 1969, *in final form* 1*st June* 1970

Abstract. A simple relation between the energy of formation E_f of Schottky defects in alkali halides and compressibility is developed. Values of E_f for alkali halides for which experimental values are not available are estimated and agree with the recent theoretical calculations.

For a vibrating atom regarded as a simple harmonic oscillator the restoring force, for displacement Δr, is given by

$$f(\Delta r) = -K\Delta r$$

so that

$$\frac{f(\Delta r)\Delta r}{(\Delta r)^2} = -K. \tag{1}$$

Since $f(\Delta r)\Delta r$ has the dimensions of energy, we can write empirically (Mukerjee 1965)

$$f(\Delta r)\Delta r = C_1 E_f \qquad \text{and} \qquad (\Delta r)^2 = C_2 v^{2/3}$$

where C_1 and C_2 are constants and v is the average atomic volume. Thus the force constant K can be written as

$$K = C_3 \frac{E_f}{V^{2/3}} \tag{2}$$

where V is the volume per mole.

Using the simplified Born–Mayer potential Mitra and Joshi (1960) have shown that in the case of ionic crystals the force constant K is given by

$$K = \frac{36 r_0}{M\chi} \qquad \text{for NaCl type crystals}$$

where r_0 is the nearest neighbour distance, M, is the co-ordination number and χ is the compressibility. On substituting proper values of r_0 and M, the above equation reduces to

$$K = \frac{3a}{\chi} \tag{3}$$

where a is the lattice constant. Combining equations (2) and (3) and remembering that a is proportional to $V^{1/3}$, we have

$$\frac{E_f}{V} = \frac{C}{\chi} \tag{4}$$

where C is a constant (here a dimensionless quantity).

Figure 1 shows the plot of E_f/V against χ^{-1} values from table 1.

The slope of the line in the figure turns out to be $3{\cdot}4 \times 10^{-13}$ so that equation (4) can be written as

$$E_f \text{ (eV)} = \frac{3{\cdot}4 \times 10^{-13} V}{\chi}. \tag{5}$$

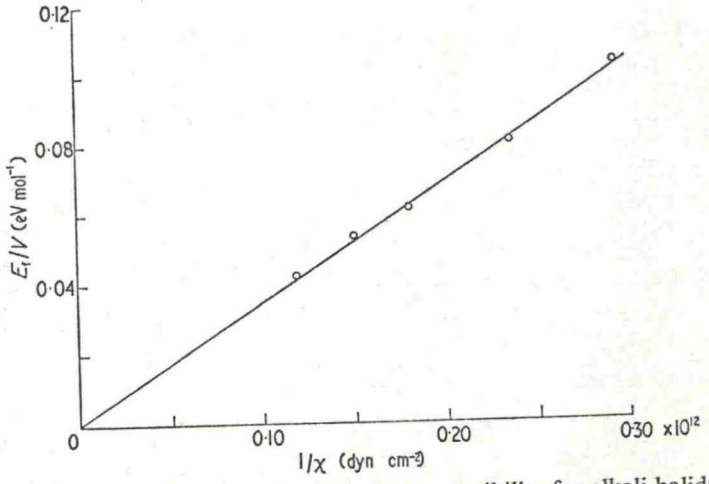


Figure 1. E_t/V against reciprocal of compressibility for alkali halides.

Table 1. Experimental values of E_t, E_t/V, compressibility χ, $1/\chi$ and $E_t\chi/V$

Crystal	E_t (eV)	E_t/V (eV mol^{-1})	$\chi \times 10^{12}$ (dyn^{-1} cm^2)	$10^{12}/\chi$ (dyn cm^{-2})	$E_t\chi/V$
LiF	2·34	0·235	1·17	0·855	0·27
	2·68[a, b, c]	0·269			0·32
LiCl	2·12[a]	0·103	3·41	0·293	0·35
NaCl	2·17[d]	0·080	4·26	0·235	0·34
KCl	2·26[e]	0·060	5·63	0·178	0·34
KBr	2·30[f]	0·053	6·70	0·149	0·35
KI	2·21[g]	0·042	8·54	0·117	0·36

a, Haven (1950); b, Barsis *et al.* (1967); c, Stoebe and Praat (1967); d, Allnatt and Pantelis (1968); e, Beaumont and Jacobs (1966); f, Barr and Dawson (1970); g, Chandra and Rolfe (1970); h, Born and Huang (1954).

The values of E_t estimated from equation (5) for those alkali halides for which reliable experimental values are not available, are given in table 2. The experimental values of E_t for LiBr, LiI and NaBr probably need redetermination (Barr and Lidiard 1969). These

Table 2. Values of E_t estimated from equations (5), (6) and (7) and comparison with available values

Crystal	$\chi \times 10^{12}$† (dyn^{-1} cm^2)	E_t (eV) equation (5)	E_t (eV) (Boswarva and Lidiard)	E_t (eV) equation (6)	E_t (eV) equation (7)	E_t (eV) (Rao and Rao)
LiBr	4·31	1·98	1·323	4·79	1·75	—
LiI	6·01	1·86	1·004	4·47	1·54	—
NaF	2·11	2·42	2·491	2·58	2·60	—
NaBr	5·08	2·15	1·916	2·26	2·20	—
NaI	7·07	1·97	1·603	2·63	1·98	—
KF	3·30	2·41	2·419	3·26	2·47	—
RbF	4·10	2·25	2·257	3·22	2·21	—
RbCl	6·65	2·24	2·243	2·53	2·11	2·17
RbBr	7·94	2·11	2·112	2·63	2·04	1·99
RbI	9·57	2·12	1·965	2·58	1·96	1·88

† Born and Huang (1954).

salts are therefore included in table 2; column 4 of this table gives the nearest theoretical values of E_f calculated by Boswarva and Lidiard (1967).

An explicit expression for E_f derived by Mullen (1966) in terms of the elastic and dielectric constants is

$$E_f = E_L - \left(\frac{8{\cdot}27e^2}{\kappa r_0^4}\right)\left\{\alpha_+ + \alpha_- + \frac{2e^2}{k_s}\left(1-\frac{1}{\kappa}\right)\right\} \tag{6}$$

where E_L is the lattice energy per pair of ions, κ the dielectric constant, r_0 the nearest neighbour distance, α_+, α_- electronic polarizability of the positive and negative ions and k_s is the Einstein spring constant which is equal to $2r_0C_{\parallel}$ where $C_{\parallel}$ is the usual elastic coefficient associated with the longitudinal vibrations which propagate along a cube axis. The theory is based on the Einstein model of an ionic solid and ion correlations are treated as a perturbation. It is assumed in the theory that the effective dielectric constant can be represented by the static dielectric constant and that the Einstein model gives relaxed displacements correct to first order.

An empirical relation (Barr and Lidiard 1969)

$$E_f = 2{\cdot}14\times10^{-3}T_m \text{ (eV)} \tag{7}$$

is found useful in practice and gives results to within 10%.

Recently Rao and Rao (1968) have calculated the values of E_f for RbCl, RbBr and RbI using a high van der Waals term in the potential energy expression. Their values as well as those calculated from equations (6) and (7) are included in table 2.

Acknowledgments

Financial support of the Ministry of Education, Government of India, to one of us (NGV) is gratefully acknowledged.

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