Majority and minority intrinsic defects in lithium and sodium halides

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Abstract. We present new findings on the enthalpies of formation of vacancies and interstitial ion defects on either sublattice in the alkali halide crystals MX (X = F, Cl, Br and M = Li, Na) using the MPPI model. The model uses a minimum fit to crystal properties and is fully consistent with the dielectric response. The role of the non-Coulombic short range forces *vis-a-vis* polarization fields in the stabilization of the defect formation process is examined and discussed in detail. It is shown that it is important to treat the electrostatic polarization caused by the point defect carefully and variation in potential modelling has a comparatively minor effect on the calculations of enthalpies of formation.

Keywords. Vacancies; interstitials; formation enthalpies; alkali halides; crystal potential models; polarization models.

1. Introduction

Charge and matter transport studies in the crystals of the alkali halide family have been invariably interpreted in terms of a dominant Schottky disorder without any interstitial component on either sublattice. In the light of the current levels of sophistication in the measurement techniques as well as in the analysis of transport data, it has been recently speculated that there could be a sizeable contribution from interstitials even in these materials (Jacobs and Vernon 1994). The formation enthalpy of the Schottky defect in alkali halides is well quantified both by experiments and theoretical calculations. However the bulk of these calculations overstress the role of the potential parameters, which are found by extensive fitting to crystal properties (Sangster *et al* 1978).

In this paper we present our findings on the formation enthalpies of the Schottky as well as Frenkel defects, using the modified polarizable point ion (MPPI) model (Murti and Banhatti 1993) and a two-body short-range potential model, whose parameters are minimally fitted to crystal properties. We present detailed comparison on NaCl with a previous work also based on MPPI model (Murti and Usha 1976; Usha 1976) but using the Tosi potential (Tosi 1964). By this attempt we wish to highlight the larger importance of the polarization model for ionic crystals as against subtle refinements in the potential model.

2. Potential models

In the construction of a two-body potential model with the short-range interactions given by the expression

$$\phi_{ij}(r) = A_{ij} \exp \left[-\frac{r_{ij}}{\rho_{ij}} \right] - \frac{C_{ij}}{r_{ij}^6}, \quad (1)$$

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we need to obtain nine parameters, namely the repulsion parameters A_{ij} and ρ_{ij} and the van der Waals (vdW) coefficients C_{ij} . The short range parameters were obtained in the shell model schemes by fitting to six independent bulk properties, namely three elastic constants, lattice constant r_0 and the static or high frequency dielectric constants as well as the transverse optical phonon frequency. Of these, the elastic constant equations use the first and second derivatives of the potential and to extract each of the potential parameters without introducing arbitrariness is difficult. The vdW parameters are taken from Mayer's (1933) type of calculations.

Alkali halides are simpler to deal with since they are closed shell ionic systems. The Coulomb part is well represented by the Madelung potential. For the non-Coulombic part, one can then use the calculations of the type made by Gordon and Kim (1972) (GK), Cohen and Gordon (1979) and Macrodt and Stewart (1979), which are based on an electron gas model. The correlation energy is however poorly estimated by this model. Hence, we have been constrained to consider the GK data for lithium and sodium halides, where we expect the vdW type of forces to be small and can be easily identified and eliminated when one fits the data to an exponential form. Using the values of A_{ij} and ρ_{ij} in the equilibrium lattice condition, as well as the interrelation between the C_{ij} s, we determine the vdW parameters. These correspond to the Set III parameters of our potential model (Banhatti *et al* 1991). Working within the MPPI scheme, we determine the electronic polarizabilities (α_c and α_a) using the experimental value of the static dielectric constant and the displacement polarizability α_d determined from the short range interactions (Banhatti and Murti 1993). These are tabulated in tables 1 and 2.

The vdW coefficients of the lithium halides turn out to be quite negligible as expected and are hence set to zero. The values of $\alpha_{c,a}$ are small in the lithium halides and α_d are large. These may well result in larger ion relaxations around the defects.

Table 1. Overlap repulsion parameters (electron gas model).

Crystal	LiF	LiCl	LiBr	NaF	NaCl	NaBr
$A_{CC}(10^3 \text{ eV})$	2.0260	2.0260	2.0260	45.7200	45.7200	45.7200
$A_{CA}(10^3 \text{ eV})$	0.6724	0.7901	0.8713	2.5504	1.7363	1.8256
$A_{AA}(10^3 \text{ eV})$	2.2431	1.2272	2.9482	2.2431	1.2272	2.9482
$\rho_{CC}(\text{\AA})$	0.1215	0.1215	0.1215	0.1422	0.1422	0.1422
$\rho_{CA}(\text{\AA})$	0.2508	0.2991	0.3144	0.2435	0.3049	0.3193
$\rho_{AA}(\text{\AA})$	0.2494	0.3214	0.3320	0.2494	0.3214	0.3320

Table 2. van der Waals coefficients and dipole polarizabilities. C's are in $\text{eV \AA}^6$ and α 's are in $\text{\AA}^3$.

Crystal	C_C	C_{CA}	C_{AA}	α_c	α_A	α_d
LiF	0.00	0.00	0.00	0.002	0.028	1.378
LiCl	0.00	0.00	0.00	0.017	0.465	2.864
LiBr	0.00	0.00	0.00	0.032	0.032	3.341
NaF	1.307	0.517	0.812	0.100	0.294	1.448
NaCl	3.725	3.693	13.758	0.149	1.032	2.607
NaBr	5.327	6.119	28.341	0.181	1.563	3.045

Table 3. Energy contributions (eV) to the defect formation enthalpy in NaCl.

Defect	Vacancy				Interstitial			
	Cation		Anion		Cation		Anion	
	(1) s_a	(2) s_a	(1) s_c	(2) s_c	(1) s_a	(2) s_a	(1) s_c	(2) s_c
$s_{a/c}$	0.08	0.08	0.09	0.09	0.14	0.16	0.18	0.19
W_{rl}	8.02	7.95	8.00	8.10	2.07	2.98	4.27	4.42
W_{co}^1	-2.06	-2.06	-2.27	-2.27	-3.00	-3.32	-3.51	-3.63
W_{sr}^{rep}	1.01	1.08	1.22	1.21	1.14	0.79	-0.38	-0.28
W_{sr}^{vdw}	-0.04	-0.05	-0.05	-0.06	0.03	-0.04	0.17	0.13
W_p^1	-0.06	0.05	0.21	0.18	-0.20	-0.08	-0.36	-0.36
W_p^2	-1.70	-1.73	-1.79	-1.77	-1.57	-1.57	-1.57	-1.57
W_d	5.20	5.23	5.29	5.37	-1.68	-1.42	-1.71	-1.30

Table 4. Defect formation enthalpies (eV).

Defect enthalpy	LiF	LiCl	LiBr	NaF	NaCl	NaBr
h_s (eV)	2.65	1.83	1.59	3.25	2.48	2.22
h_s (eV)	2.3-2.7	2.12	1.80	2.9-3.2	2.4-2.5	2.2-2.4
h_{cF} (eV)	3.83	2.60	2.40	4.69	3.52	3.26
h_{aF} (eV)	4.75	3.16	3.84	5.06	3.58	4.14

3. Defect formation energies

Working within the MPPI scheme of polarization, we have estimated the formation energies for the different defects using two potential sets. The various energy contributions are shown in table 3. The column (1) corresponds to our recent Set III potential and the column (2) of the results corresponds to the potential of Murti and Usha (1976).

We note that the equilibrium displacements (s_a or s_c) hardly change from one potential set to the other in the case of the vacancy defects. The differences in most of the terms (the rigid lattice energy W_{rl} , the Coulomb term W_{co}^1 , the short range terms W_{sr} and the second region polarization energy W_p^2) are merely marginal and do not finally affect the vacancy formation energy W_a in any significant way. One term where there is a marked change is the region 1 polarization energy W_p^1 where as a result of potentials, the dipole polarizabilities are different. In the case of the cation interstitial, the effect of differences in short range potentials is likely to be more pronounced since the defect is contained in a smaller volume of region 1 and hence there exist marked differences in some of the energy terms.

The formation enthalpies of Schottky disorder (h_s), cationic Frenkel disorder (h_{cF}) and anionic Frenkel disorder (h_{aF}) are shown in table 4 for the six salts, along with the experimental values of h_s . It may be seen that the calculated values of h_s obtained using the MPPI model are in good agreement with the experimental values. This suggests that with the low effective dipole polarizabilities of ions in these salts, the MPPI model is adequate. Further, the minority defect enthalpies are much larger than the majority

defect enthalpy by values ranging between 0.8 eV–2.0 eV. This is a significant finding which makes the possibility of the minority defects playing a significant role in transport processes in these crystals quite remote.

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