# Barrier Heights to Ion Migration in Alkali Halides

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Shell model calculations have been carried out to estimate the barrier heights to migration of ions in alkali halides by employing Sangster's parameters. The calculated values are in good agreement with experiment.

## *Introduction*

It is important to understand the mechanism of ion movement in ionic solids in order to interpret ionic conductivity and diffusion data[1, 2]. Ionic lattice calculations employing the Polarizable-Point Ion (ppi) model on several alkali halides have been carried out by several workers to obtain theoretical estimates of the barrier heights to migration of ions[1–3]. Recent studies[4–6] on defect properties of ionic solids have, however, shown the limitations of the ppi method and the importance of employing a larger, explicitly relaxed region of ions. We, therefore, considered it worthwhile to carry out shell model calculations[5] on the energy of migration of ions in alkali halides using a larger region I. In doing so, we thought it appropriate to employ the consistent shell model parameters derived by Sangster[7] for alkali halides of rock-salt structure. These parameters have the important property that they are characteristic of individual ions irrespective of the salt they form. Sangster and Dixon[8] have further reported the corresponding set of potential parameters using the Born-Mayer form of the potential with Pauling's radii.

In our calculations, we have employed the generalised Mott-Littleton procedure with the defect region sufficiently large to eliminate the effect of its size on the calculated defect parameters. We have used the HADES program of Norgett for these calculations. The saddle point configurations for migration employed were the same as those described in earlier publications from this laboratory[3, 9].

## *Results and Discussion*

In the case of KCl, we have examined ion migration through isolated vacancies, vacancy pairs and interstitials, the last being relevant to high temperature behaviour of alkali halides[3]. The calculated barrier heights to migration in KCl by the isolated vacancy mechanism are 0.81 and 1.16 eV for cation and anion respectively, values which are close to the experimentally observed barrier heights[1–3, 9]. The barrier heights by the vacancy pair mechanism are significantly higher than those by the single vacancy mechanism. The formation energies of cation and anion Frenkel defects in KCl are 3.27 and 3.95 eV respectively. These values are close to those reported by Schulze and Hardy[10] employing the lattice statics and deformation dipole model. The migration energy for collinear interstiticaly mechanism are, however, quite low (0.32 and 0.27 eV for cation and anion respectively) indicating that this mechanism may indeed become important at high temperatures as suggested elsewhere[3].

Table 1. Energies of formation of Schottky defects and migration[a] of vacancies in alkali halides.

| | $E_\mathrm{s}$ | $E_\mathrm{m}^{\mathrm{v}+}$ | $E_\mathrm{m}^{\mathrm{v}-}$ |
|---|---|---|---|
| NaCl | 2.25<br>(2.18–2.38 [b]) | 0.81<br>($0.71 \pm 0.05$ [b]) | 1.16<br>($1 \pm 0.1$ [b]) |
| KCl | 2.33<br>($2.28 \pm 0.02$ [b]) | 0.88<br>($0.71 \pm 0.12$ [b]) | 0.92<br>($0.99 \pm 0.04$ [b]) |
| RbCl | 2.43<br>(2.12 [c], 2.04 [d]. 2.44 [e]) | 0.87<br>(0.93 [c], 0.54 [d]) | 0.90<br>(1.45 [d]) |
| KBr | 2.38<br>(2.3–2.53 [b]) | 0.82<br>(0.62–0.67 [b]) | 0.95<br>(0.87–0.95 [b]) |
| RbBr | 2.31<br>(1.98 [c]) | 0.84<br>(0.8 [c]) | 0.9<br>— |

[a] Experimental values are shown in parentheses.
[b] From Ref.[1], [c] from Ref.[9], [d] from Refs.[14, 15], [e] from Ref.[16].

Energies of formation of Schottky defects, $E_\mathrm{s}$, and barrier heights to migration by the single vacancy mechanism, $E_\mathrm{m}^{\mathrm{v}\pm}$, in several alkali halides of rock salt structure calculated by us employing the shell model are listed in Table 1. It is gratifying that, unlike the ppi model, the shell model parameters give values of defect energies close to experimental values. The study clearly demonstrates the superiority of shell model calculations in obtaining estimates of barrier heights to ion migration. Our results also show that the shell model parameters of Sangster[7, 8] can be satisfactorily employed for such calculations.

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We have carried out some preliminary calculations on ion migration in CsCl (Pm3m structure) by the single vacancy mechanism employing the parameters of Müller and Norgett[11]. We obtain a Schottky formation energy of 1.78 eV just as reported by Müller and Norgett. The anion and cation migration energies are both close to 0.4 eV. While the value of 0.4 eV is close to the experimental anion migration energy[12], it is not easy to understand the value for the cation migration; ppi calculations[13] give unreasonable values of both cation and anion migration energies in CsCl.

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