Energies of Trivalent Cation Impurity-Cation Vacancy Complexes in KCl

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Interaction energies of six trivalent cation impurity-cation vacancy configurations in KCl have been evaluated and compared with experimental data.

1. Introduction

There have been extensive theoretical and experimental[1–8] studies on divalent cation (or anion) impurity-cation (or anion) vacancy pairs in alkali halides during the last few decades. The nature of the interaction of trivalent impurity cations, M^{3+}, with cation vacancies in alkali halides is not understood and experimental studies on such systems are limited to a few recent reports on the conductivity, dielectric loss and optical spectra of M^{3+} doped alkali halides[9–12]. Introduction of M^{3+} impurity ions into the cation sublattice of KCl creates two cation vacancies for each M^{3+} impurity ion introduced. These vacancies can form complexes with the impurity ion differing in their configuration as shown in Figure 1. We have carried out calculations on the energies of association of such complexes in the $KCl:Pr^{3+}$ system in the light of the available experimental data employing the generalised formulation described elsewhere[1, 2, 13]. It may be noted that theoretical evaluations of various defect parameters such as energies of formation, association and migration of defects in ionic solids employing the Born model of cohesion have met with considerable success[1–3, 13–15] and have led to a better understanding of experimental observations.

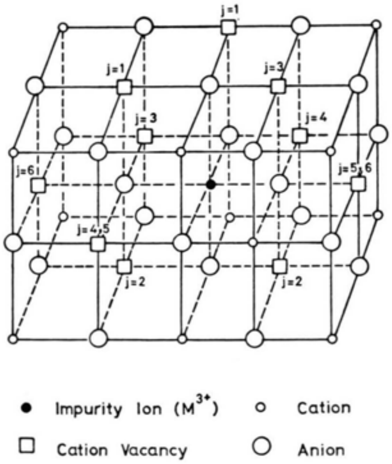

Fig. 1. NaCl lattice showing various M^{3+}-cation vacancy complexes indicated by $j=1, 2, 3, 4, 5, 6$.

2. Results and Discussion

By employing ionic radii* of 1.33, 1.63 and 1.51 Å for Pr^{3+}, Cl^- and K^+ respectively, we have obtained defect parameters for the isolated cation vacancy and Pr^{3+} impurity ion in the KCl lattice (Table 1). The results of our calculations on the various Pr^{3+}-cation vacancy associations (I – V complexes) in the $KCl:Pr^{3+}$ system are shown in Table 2.

Table 1. Parameters for isolated defects in KCl (Energies in eV).

	Cation vacancy	Pr^{3+} impurity
ξ	0.065	0.176
m	−0.050	−0.146
U_{relax}	−2.759	−15.708
U_{rl}	7.250	8.335
U_{conf}	(U_{v}^+) 4.491	(U_{i}) −7.373

The first of the I – V complexes ($j=1$), where the two cation vacancies are situated close to each other at a distance $\sqrt{2}\,r_0$ (r_0 being the interionic distance), is not favoured from energy considerations since vacancies with equal effective charge repel each other. Our calculations show that this type of associated complex cannot exist since it is less stable than the respective isolated defects. In the other five complexes the two charge compensating vacancies are separated by distances of $2\,r_0$ ($j=2$), $\sqrt{6}\,r_0$ ($j=3$), $\sqrt{8}\,r_0$ ($j=4$), $\sqrt{10}\,r_0$ ($j=5$) and $4\,r_0$ ($j=6$). On multiplying the calculated energy values for these associated states, E_j^{IV}, with their respective Z_l (total number of equivalent configurations), we obtain the net association energy $\langle E_j^{\text{IV}} \rangle$ for these complexes. If we do so, we find that the fifth associated state ($j=5$), in which one vacancy is at a nearest neighbour (nn) site and the other at a next-nearest-neighbour (nnn) site relative to the Pr^{3+} ion, is the most favoured one. This is in conformity with the experimental observations of Radhakrishna et al.[11]. On the basis of our calculations, the order for the different as-

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* The value of the radius for the Pr^{3+} ion (1.33 Å) was derived from the crystallographic data of Zachariasen[16] so as to be in conformity with the ionic radii given by Tosi[17] for Cl^- (1.63 Å) and K^+ (1.51 Å).

Table 2. Parameters for I−V complexes in KCl (Energies in eV).

	$j=1$		$j=2$		$j=3$		$j=4$		$j=5$		$j=6$	
ξ_k	(100)	0.142	(100)	0.158	(100)	0.162	(100)	0.156	(100)	0.190	(100)	0.179
	(001)	0.132	(010)	0.174	(010)	0.161	(001)	0.176	(010)	0.180	(010)	0.168
	$(\bar{1}00)$	0.279	(001)	0.177	$(0\bar{1}0)$	0.170	(210)	0.047	(001)	0.174	(300)	0.059
	$(00\bar{1})$	0.161	$(0\bar{1}0)$	0.176	(200)	0.046	(111)	0.076	$(\bar{1}00)$	0.169	(210)	0.051
	(201)	0.054	(210)	0.050	(120)	0.045			(300)	0.049		
	(111)	0.136	(120)	0.071	(111)	0.,071			$(\bar{1}20)$	0.054		
	(102)	0.038	(111)	0.042	$(11\bar{1})$	0.084						
	$(1\bar{1}1)$	0.061										
m_k	(100)	−0.130	(100)	−0.118	(100)	−0.131	(100)	−0.122	(100)	−0.161	(100)	−0.148
	(001)	−0.144	(010)	−0.134	(010)	−0.162	(001)	−0.184	(010)	−0.159	(010)	−0.143
	$(\bar{1}00)$	−0.161	(001)	−0.187	$(0\bar{1}0)$	−0.153	(210)	−0.045	(001)	−0.156	(300)	−0.053
	$(00\bar{1})$	−0.151	$(0\bar{1}0)$	−0.180	(200)	−0.031	(111)	−0.049	$(\bar{1}00)$	−0.149	(210)	−0.046
	(201)	−0.050	(210)	−0.048	(120)	−0.048			(300)	−0.050		
	(111)	−0.089	(120)	−0.047	(111)	−0.044			$(\bar{1}20)$	−0.046		
	(102)	−0.041	(111)	−0.051	$(11\bar{1})$	−0.047						
	$(1\bar{1}1)$	−0.047										
U_{relax}	−12.087		−11.742		−11.088		−10.830		−13.100		−14.949	
U_{rl}	13.749		12.676		12.379		12.006		13.607		15.077	
$U_{\text{conf}}^{\text{IV}(j)}$	1.662		0.934		1.291		1.176		0.507		0.128	
E_j^{IV} (a)	−0.053		0.675		0.318		0.433		1.102		1.481	
Z_l	16		6		12		6		8		3	
$\langle E_j^{\text{IV}} \rangle$	−0.848		4.050		3.816		2.598		8.816		4.443	

(a) The association energies are evaluated as follows: $E_j^{\text{IV}} = 2\,U_{\text{v}}^{+} + U_{\text{i}} - U_{\text{conf}}^{\text{IV}(j)}$.

sociated states works out to be fifth > sixth > second > third > fourth. It is noteworthy that Radhakrishna et al.[11] have analysed their experimental data in the light of the fourth, fifth and sixth associated state of these I − V complexes.

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