



SEMI-EMPIRICAL SIMULATIONS OF F-CENTER DIFFUSION IN KCl CRYSTALS

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Abstract—The semi-empirical method and 224 atom quantum clusters were used for calculating the activation energy for diffusion of cation and anion vacancies and F-centers in KCl crystals. The relevant activation energies of 1.19 eV, 1.44 eV and 1.64 eV, respectively agree well with the experimental data. Copyright © 1996 Elsevier Science Ltd

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1. INTRODUCTION

The study of mobility of crystal lattice defects and of the diffusion processes associated with point defect is of great importance for understanding the kinetics and mechanism of primary radiation-induced defect survival, aggregation and recombination luminescence.

It has been firmly established by numerous investigations that in alkali halides interstitial halogen ions and atoms (called I- and H-centers, respectively) are stable only at low temperatures ($T < 60$ K) [1]. Their annealing at higher temperatures controlled by their diffusion and elastic interactions leads to a series of secondary defect-controlled reactions, which have been extensively studied, both experimentally [1] and theoretically [2-4].

The counterparts of mentioned I, H-centers are anion vacancies, V_a , and those with a trapped electron (F-centers). They are much more stable defects and thus their diffusion becomes a significant phenomenon at much higher temperatures. Another important point defect is cation vacancy, V_c .

There are no doubts that V_a are much more mobile defects as compared to F-centers [1, 5, 6]. As it is shown in [5, 6], V_a -induced effects are observed already at $T > 220$ K in KCl. In particular, this comes out from the decay of V_a absorption (the so-called α -band), destruction of activator Ag^0 -centers (known to be stable up to 370 K), increased efficiency of the creation of complex centers known as F_2^+ , M, F_A , Z, U, $Tl^0 V_a$, etc. ([5, 6] and references therein). The activation energy for V_c and V_a migration has been estimated using a number of different techniques including radioactive tracers, ionic conductivity, etc. They are collected in Table 1. As one can see, the

average activation energy for V_c and V_a diffusion are about 0.70 eV and 1.0 eV, respectively. As to the F-centers, they start to migrate at higher temperatures. Based on thermal formation and destruction of colloid centers, these temperatures were estimated to fall into the interval 470–530 K [5]. The experimentally estimated activation energy for F-center diffusion considerably varies from the paper to paper [16]. We plotted in Table 1 results of the most 'direct' methods of its evaluation (mobility measurements under electrolytic coloration, diffusion studies in additively colored crystals); they center around 1.5 eV.

In the recent years, a number of calculations were done on the activation energies for defect diffusion employing mainly a shell model and the relevant HADES computer code employing di-atomic potentials [22]. However, this technique obviously does not allow us to treat F-centers due to the essentially quantum nature of the electron inside an anion

Table 1. The summary of experimental and theoretical diffusion energies (in eV) for cation (V_c) and anion (V_a) vacancies, and F-centers in KCl crystals. Results of the present study are marked by asterisk*

V_c	V_a	F-center
	Experimental	
0.67 [7]	0.83 [13]	1.59 [16]
0.73 [8]	0.89 [9]	1.30 [17]
0.73 [9]	0.89 [12]	1.35–1.65 [18]
0.74 [10]	0.95 [14]	1.40 [19]
0.75 [11]	0.99 [8]	1.61 [20]
0.76 [12]	1.04 [15]	
	1.11 [10]	
	1.19 [11]	
	Theoretical	
—	0.95 [21]	2.23 [21]
1.19*	1.44 *	1.64 *

vacancy. To our knowledge, the only theoretical study of F-center diffusion in KCl has been performed in Ref. [21]. This was based, essentially, on a one-electron approximation.

In this paper, we present results for both V_c , V_a and F-center obtained in terms of the same and more sophisticated formalism.

2. METHOD AND RESULTS

The modified semi-empirical method of the Intermediate Neglect of Differential Overlap (INDO) has been used combined with as large as 224-crystalline site quantum cluster embedded into the electrostatic field of non-point charges of the rest of a crystal [23]. That is, the electronic density of atoms of the rest of a crystal is explicitly taken into account when calculating matrix elements of Coulomb interactions of these atoms with cluster atoms. This C_{2v} -symmetry clusters includes several spheres of atoms surrounding both V_a and regular Cl ions along the (110) axis with which an exchange of positions occurs. Use of such big cluster permits the avoidance of potential influence of the boundary conditions imposed on the quantum cluster. The relevant computer code SYM-SYM is

based on the complete use of cluster symmetry and is described in Ref. [24]. The valence basis set includes 3s, 3p atomic orbitals (AOs) of Cl-ions and 4s, 4p AOs on K^+ that is, we solve essentially many-electron problems. Recently this method with the same parameters has been successfully applied to the simulations of the diffusion hops of self-trapped holes in KCl crystals [25]. In V_a (F) center calculations one of regular Cl atoms in the cluster center was removed and then (in the case of F-center) one electron added to the cluster. No *a priori* pattern of the electronic density distribution is assumed, this is obtained as a result of the self-consistent field (SCF) calculation of the electronic structure. Most of cluster ions were allowed to relax in order to achieve a minimum of the total energy of the system. This automated option is incorporated into SYM-SYM code used here.

Tables 2 and 3 show the calculated optimized equilibrium coordinates and saddle-point atomic configurations for V_c , V_a and F-center. For a charged empty vacancy, six cations surrounding it are displaced outwards by five percent of the interatomic (K-Cl) spacing, a_0 . The effective charges of ions surrounding V_a and far from it are rather close, approximately $\pm 0.75e$. This demonstrates that a

Table 2. Diffusion of cation V_c and anion vacancy V_a in KCl crystal. Coordinates of atoms are given in units of a perfect K-Cl spacing a_0 . Effective charges in units e . Only one atom from a set of the equivalent by symmetry atoms is presented. N is the number of equivalent atoms

Anion vacancy										
N	Equilibrium configuration				Saddle-point configuration					
	Ion vac	Coordinates			Charge on ion	Ion vac	Coordinates		Charge on ion	
		0.50	-0.50	0.00	0.00		0.50	-0.50	0.00	0.00
1	Cl	-0.47	0.47	0.00	-0.752	Cl	0.00	0.50	0.00	-0.761
2	K	0.50	0.55	0.00	0.748	K	0.59	0.64	0.00	0.744
2	K	1.54	-0.49	0.00	0.748	K	1.46	-0.47	0.00	0.748
2	K	-0.50	1.50	0.00	0.748	K	-0.49	1.53	0.00	0.751
2	Cl	0.50	1.50	0.00	-0.750	Cl	0.49	1.55	0.00	-0.756
2	Cl	1.48	0.48	0.00	-0.754	Cl	1.52	0.50	0.00	-0.753
2	Cl	1.47	-1.47	0.00	-0.754	Cl	1.45	-1.45	0.00	-0.751
1	Cl	-1.49	1.49	0.00	-0.751	Cl	-1.46	1.46	0.00	-0.754
2	K	-0.51	0.51	1.01	0.747	K	-0.52	0.52	1.01	0.749
2	K	0.50	-0.50	1.04	0.749	K	0.50	-0.50	0.90	0.747
Cation vacancy										
N	Equilibrium configuration				Saddle-point configuration					
	Ion vac	Coordinates			Charge on ion	Ion vac	Coordinates		Charge on ion	
		0.50	-0.50	0.00	0.00		0.50	-0.50	0.00	0.00
1	K	-0.47	0.47	0.00	0.751	K	0.00	0.00	0.00	0.766
2	Cl	0.50	0.55	0.00	-0.746	Cl	0.58	0.64	0.00	-0.755
2	Cl	1.54	-0.49	0.00	-0.747	Cl	1.51	-0.49	0.00	-0.748
2	Cl	-0.51	1.50	0.00	-0.747	Cl	-0.50	1.53	0.00	-0.745
2	K	0.50	1.50	0.00	0.746	K	0.49	1.54	0.00	0.749
2	K	1.48	0.48	0.00	0.751	K	1.51	0.50	0.00	0.749
2	K	1.47	-1.47	0.00	0.751	K	1.47	-1.47	0.00	0.749
1	K	-1.49	1.49	0.00	0.748	K	-1.47	1.47	0.00	0.749
2	Cl	-0.51	0.51	1.01	-0.749	Cl	-0.49	0.49	0.99	-0.746
2	Cl	0.50	-0.50	1.04	-0.748	Cl	0.49	-0.49	0.99	-0.751

Table 3. Diffusion of F-center in KCl crystal. Coordinates of atoms are given in units of a perfect K-Cl spacing a_0 . Effective charges in units e . Only one atom from a set of the equivalent by symmetry atoms is presented

Equilibrium configuration				Saddle-point configuration					
Ion	Coordinates			Charge on ion	Ion	Coordinates			Charge on ion
V_a	0.50	-0.50	0.00	0.00	V_a	0.50	-0.50	0.00	0.00
					V_a	-0.50	0.50	0.00	0.00
Cl	-0.48	0.48	0.00	-0.747	Cl	0.00	0.00	0.00	-0.743
K	0.50	0.52	0.00	0.642	K	0.59	0.63	0.00	0.670
K	1.52	-0.50	0.00	0.672	K	1.42	-0.47	0.00	0.720
K	-0.50	1.50	0.00	0.741	K	-0.49	1.50	0.00	0.693
Cl	0.50	1.51	0.00	-0.747	Cl	0.50	1.55	0.00	-0.752
Cl	1.49	0.49	0.00	-0.749	Cl	1.53	0.51	0.00	-0.750
Cl	1.48	-1.48	0.00	-0.750	Cl	1.46	-1.46	0.00	-0.748
Cl	-1.50	1.50	0.00	-0.750	Cl	-1.48	1.48	0.00	-0.751
K	-0.51	0.51	1.00	0.731	K	-0.48	0.48	0.99	0.688
K	0.50	-0.50	1.02	0.668	K	0.48	-0.48	0.95	0.704

certain deviation from the purely ionic model of the chemical bonding in KCl ($\pm 1e$) takes place. The activation energy for diffusion is the difference of total energies for optimized equilibrium and saddle point-configurations. For V_c the calculated activation energy is 1.19 eV, for V_a this quantity is found to be 1.44 eV—both are larger than the average estimate of the experimental data plotted in Table 1.

In the case of the neutral F-center, the outward relaxation of surrounding cations is essentially less than for V_a , it is 0.02 a_0 only. The portion of the electron within a sphere centered on the vacancy with the radius of a_0 is 0.6 e . It is smaller than observed experimentally by means of ESR [26] and is caused by the rather narrow basis set. In the calculations of optical properties of F-centers it could easily be improved by introducing additional 1s, 2p-type AOs centered on a vacancy [27]. However, it is no longer correct in the simulations of *diffusion* since in this case one has *one* set of such 1s, 2p AOs in the equilibrium state and *two* sets—in the saddle-point, that is, two different basis sets as a result. The Cl atom in the saddle point has the effective charge similar to that in the lattice site. The resulting activation energy for F-center diffusion is 1.64 eV—in a very good agreement with the experimental data and much better than the previous one-electron calculation (2.23 eV [21]).

Considerable difference in the activation energies for V_a and F is not just a result of the 'geometrical factor', i.e. the shorter distance d for Cl atom hop to the vacancy in the former case. As follows from our calculations, in fact $d = 0.97\sqrt{2}a_0$ and $0.98\sqrt{2}a_0$ in these two cases, respectively, i.e. their relative difference is rather small (one percent of the distance between two regular lattice sites).

3. CONCLUSIONS

For the first time using the same quantum-chemical method we have calculated and compared the

activation energies for the diffusion of empty cation and anion vacancies and V_a with a trapped electron (F-center). The F-center diffusion energy exceeds that for anion vacancy, in a good agreement with the experiments. This study encourages us for the computer simulations of more complex defect migration and transformation above the room temperature, which is now in progress. Certain disagreement between experimental and calculated activation energies could be a result of the underestimate of the electronic polarization—the effect well-known for the used semi-empirical INDO method. Now we are trying to incorporate the polarization effects *a posteriori* using, for this purpose, a shell model [28].

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