Z_1 Center Orientations and Adsorption of Atomic Halogens at the (001) Surfaces of Alkali Chloride Crystals: DFT Calculations

A.S. Shalabi, Ibrahim A.Z. Al-Ansari, Amina S. Algaber

Department of Chemistry, Qatar University, Qatar

توزيعات مراكز التشوه Z_1 وادمصاص ذرات الهالوجينات على اسطح (001)

لبلورات الكلوريدات : حسابات نظرية دالة الكثافة

أحمد س. شلبي، إبراهيم أحمد الأنصاري، أمينة س. الجابر

قسم الكيمياء، كلية العلوم، جامعة قطر، ص . ب : ٢٧١٣، الدوحة - قطر

تم فحص درجات الاستقرار النسبي لتوزيعات مركز التشوه Z_1 على أسطح البلورات الايونية LiCl, NaCl, KCl المطعمة بأيونات Be^{2+}, Mg^{2+}, Ca^{2+} بالأضافة إلى تأثيراته على ادمصاص الهالوجينات (F, Cl, Br, I, At) باستخدام نموذج العناقيد المغمورة وحسابات نظرية دالة الكثافة، ثم إحاطة العناقيد المغمورة بشحنات أيونية جزئية لمكافأة جهود كولومب على مركز السطح الايوني لمضاهاة جهود ماديلونج للسطح العائل.

بناء على هذه الدراسة وجد أن التوزيعات غير الخطية للأسطح المطعمة بأيونات Mg^{2+}, Ca^{2+} أكثر استقراراً من مثيلاتها الخطية، كما يقترح أن يكون مركز التشوه Z_1 عبارة عن مركز F تحت تأثير فراغ كاتيوني مجاور أحادي التكافؤ، بغض النظر عن موقع الشائبة الكاتيونية ثنائية التكافؤ. كما وجد أن درجات الاستقرار النسبي لا تعتمد على نوع الشائبة الكاتيونية ثنائية التكافؤ أو نوع الكاتيون العائل أحادي التكافؤ، وثبت أن مركز Z_1 يغير من طبيعة الادمصاص الهالوجيني من فيزيائي إلى كيميائي. وجد أيضاً أن طاقة الادمصاص تتناسب طردياً مع درجة سالبيه الهالوجين المدمص وعلى شحنة النواة المؤثرة للكاتيون العائل.تلعب ميكانيكية الازدواج المغزلي دوراً هاماً في عملية الادمصاص، كما وجد أن الأسطح العازلة تتحول إلى أسطح شبه موصلة تحت تأثير مركز التشوه Z_1.

Keywords: *Z_1 Center-Alkaline Earth Metals-Adsorption-Atomic Halogens-DFT Calculations.*

ABSTRACT

An attempt has been made to examine the relative stabilities of Z_1 center orientations at the surfaces of Be^{2+}, Mg^{2+} and Ca^{2+} doped LiCl, NaCl and KCl ionic crystals as well as the effects of Z_1 center on the adsorption of atomic halogens (F, Cl, Br, I and At) using an embedded cluster model and density functional theory calculations. The embedded clusters were terminated by partial ionic charges that make the Coulomb potentials at the central surface sites equal to the Madelung potentials of the host surfaces. While the linear orientations of the Be^{2+} doped surfaces were more stable than the non linear orientations, the non linear orientations of Mg^{2+} and Ca^{2+} doped surfaces were more stable than the linear orientations. The Z_1 center is suggested to be an F center strongly perturbed by a neighboring monovalent cation vacancy and almost independent on the position of the divalent cation impurity. The relative stabilities were neither dependent on the type of the divalent cation impurity nor the type of the monovalent host cation. The Z_1 center changes the nature of atomic halogen adsorption from physical adsorption to chemical adsorption and the adsorption energies are directly proportional to the electronegativity of the halogen and the effective nuclear charge of the host cation. The spin pairing mechanism plays the dominant role in the course of adsorbate-substrate interactions, and the surfaces can be made semiconducting by Z_1 center imperfection.

1. Introduction

In non-irradiated alkali halide crystals, the divalent alkaline earth impurities are associated to positive ion vacancies, forming I-V electric dipoles in the <110> directions. In some cases, the vacancies are in the next nearest neighbor positions and the dipoles are oriented in the <100> directions. There are several theoretical and experimental investigation of I-V dipoles in the literature [1]. As for the monovalent impurities, it is possible to associate irradiation defects to divalent impurities. An F center associated with such I-V dipole form the Z_1 center [2]. A variety of complex aggregates or Z centers are possible. The nature of most of these is still uncertain, but the Z_1 center in KCl has been unravelled by ENDOR measurements to give two possible orientations, both of which contribute to the same optical absorption spectrum [3].

In our previous attempt to examine the relative stabilities of Z_1 center orientations at the (001) surface of LiH crystal [2], we found the linear orientation to be more stable than the non linear orientation by ca. 0.16 eV. We also found that Z_1 center could be described as an F center strongly perturbed by a neigboring positive ion vacancy V- and almost independent on the divalent impurity Be^{2+}. In the present study, we extend our investigations to include the relative stabilities of Z_1 center at the (001) surfaces of LiCl, NaCl and KCl crystals with Be^{2+}, Mg^{2+} and Ca^{2+} divalent impurities theoretically using the density functional theory model of ab initio molecular electronic structure calculations.

Theoretical and experimental studies of adsorbate-substrate interactions have become of increasing importance since they are related to a variety of technologically important processes such as catalysis, corrosion and gas sensors [4]. Several theoretical studies have been done to simulate adsorption of simple systems on ionic surfaces [5]. These ionic surfaces are known to be highly stable and the nature of adatom surface interactions are not so clear. In the present study, we have also attempted to extend our previous investigations [2] to include the effects of Z_1 centers with Be^{2+}, Mg^{2+} and Ca^{2+} divalent impurities at the (001) surfaces of LiCl, NaCl and KCl crystals on the adsorption of the atomic halogens (F, Cl, Br, I and At) theoretically using the density functional theory model of ab initio molecular electronic structure calculations.

2. Methods

2.1. Crystal simulation

To simulate the (001) surfaces of LiCl, NaCl and KCl crystals we follow a procedure previously reported for LiH [6], LiF and NaH [7] and MgO [8]. Three finite crystals, each consists of 288 point charges, were first constructed. The Coulomb potentials along the X- and Y- axes of these crystals are zero by symmetry as in the host crystals. The charges on the outer shells listed in Table 1, were fitted to make the Coulomb potentials at the four central sites closely approximate the Madelung potentials of the host crystals, and to make the Coulomb potentials at the eight points with coordinates $(0, \pm R, \pm R)$ and $(\pm R, 0, \pm R)$ where R is half the lattice distance- which is 2.57 Ao for LiCl, 2.815 Ao for NaCl and 3.147 Ao for KCl- equal to zero as they should be in the host crystals. With these charges, 0.409283 and 0.800909, the Coulomb potentials in the regions occupied by the central ions are very close to those in the unit cells of the host crystals. All charged centers with cartesian coordinates $(\pm X)$, $(\pm Y)$ and $(Z > 0)$ were then elimi-

nated to generate the (001) surfaces of LiCl, NaCl and KCl crystals, each with 176 charged centers occupying the three dimensional space ($\pm X$), ($\pm Y$) and ($Z \leq 0$) as shown in Fig.1. The defect free and defect containing clusters were then embedded within the central regions of the crystal surfaces. All the electrons of the embedded clusters were included in the Hamiltonian of the ab initio calculations. Other crystal sites entered the Hamiltonian either as full or partial point charges as demonstrated in Table 1. Both diagonal and non diagonal matrix elements of the Coulomb potentials of the full and partial charges were also included in the Fock matrix.

Table 1: Specification of the finite lattice used for the crystal surface calculations. R is half the lattice distances, which is 2.57 Å for LiCl, 2.815 Å for NaCl and 3.145Å for KCl. r is the distance of the appropriate shell from the center of the lattice.

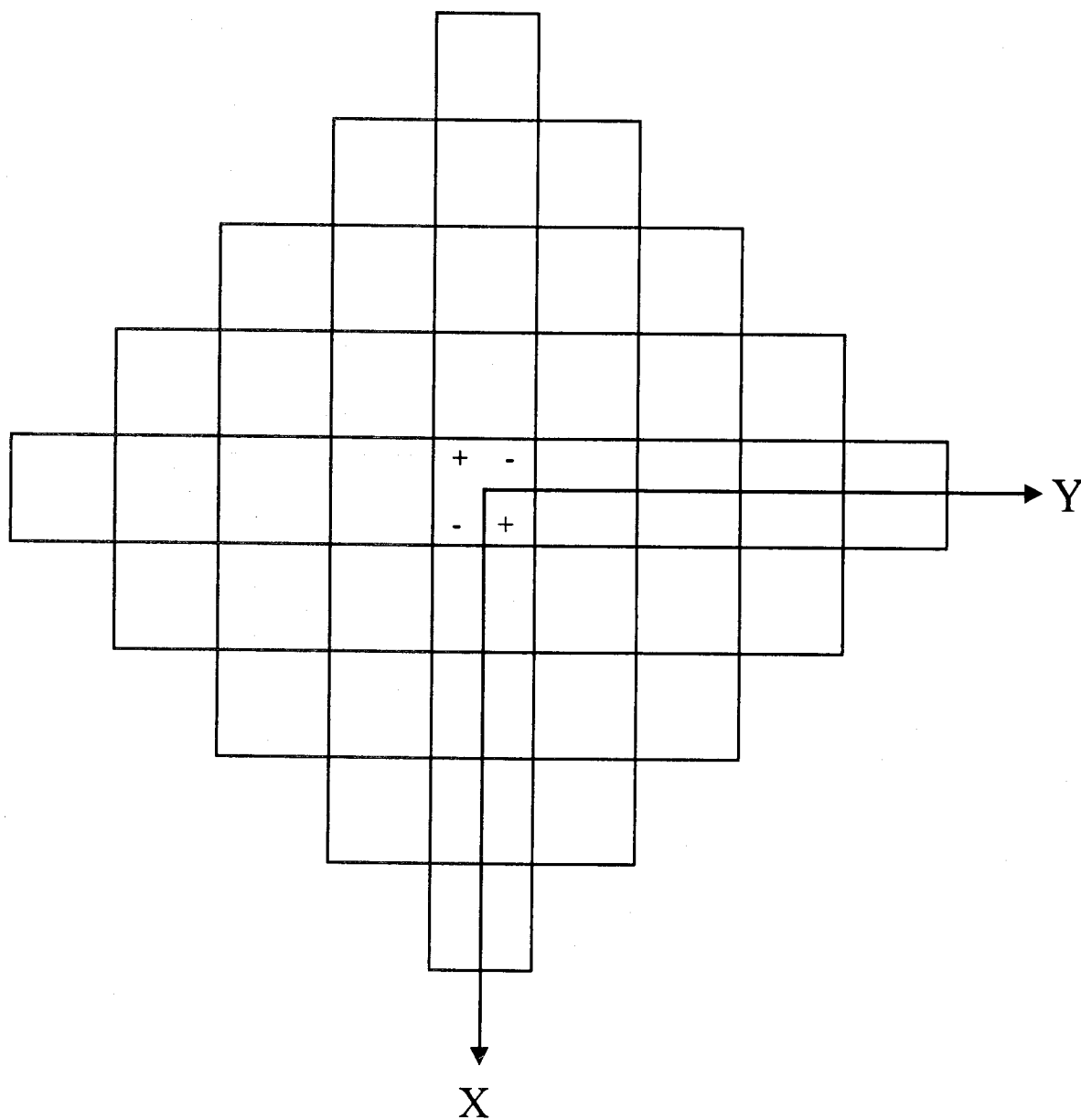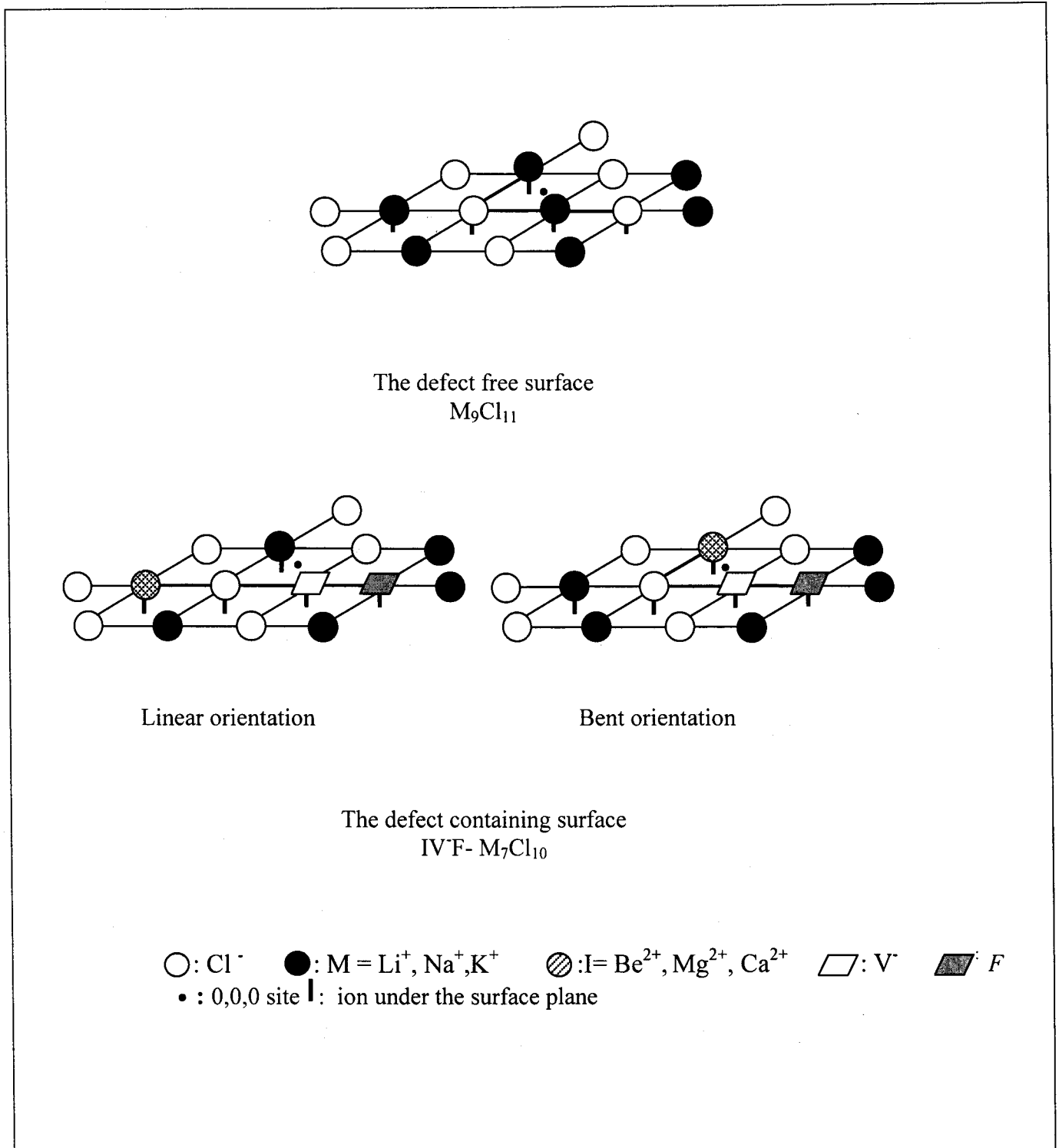| r^2/R^2	Coordinates/R $|x|,|y|,-z$			Charge $|q|$	Number of centers
2	1	1	0	1	4
6	1	1	2	1	4
10	3	1	0	1	8
14	3	1	2	1	8
18	1	1	4	1	4
18	3	3	0	1	4
22	3	3	2	1	4
26	5	1	0	1	8
26	3	1	4	1	8
30	5	1	2	1	8
34	3	3	4	1	4
34	5	3	0	1	8
38	5	3	2	1	8
38	1	1	6	1	4
42	5	1	4	1	8
46	3	1	6	1	8
50	5	5	0	1	4
50	5	3	4	1	8
50	7	1	0	1	8
54	5	5	2	1	4
54	3	3	6	1	4
58	7	3	0	1	8
66	5	5	4	1	4
54	7	1	2	0.409283	8
62	7	3	2	0.409283	8
66	1	1	8	0.800909	4
82	9	1	0	0.800909	8
86	9	1	2	0.800909	8
					$\Sigma 176$

Figure 1: Representation of the z = 0 plane of the lattice used in the calculations.

2.2 Calculations

To include the Z_1 center in the calculations, the monovalent surface cation (Li^+, Na^+ or K^+) in the central region of each crystal surface was first substituted by the divalent cation impurity (Be^{2+}, Mg^{2+} or Ca^{2+}). A second surface cation was then removed to neutralize the charge (V-), and a single electron was trapped in an adjacent anion vacancy (F center). There are, therefore, n electrons consisting of the excess (vacancy trapped) electron of the F center plus those associated with the neighboring ions. The molecular clusters representing the defect free and defect containing surfaces of LiCl, NaCl and KCl are shown in Fig.2.

The defect free surface
M_9Cl_{11}

Linear orientation   Bent orientation

The defect containing surface
IV^-F- M_7Cl_{10}

$\bigcirc$: Cl^- $\bullet$: $M = Li^+$, Na^+,K^+ $\oslash$:I= Be^{2+},Mg^{2+}, Ca^{2+} $\square$: V^- $\boxed{}$: F
$\bullet$: 0,0,0 site I : ion under the surface plane

Figure 2: The defect free and defect containing surfaces of LiCl, NaCl and KCl.

The density functional theory DFT calculations were performed using Becke three-parameter exchange functional B3 with LYP correlation functional [9]. The B3LYP hybrid functional includes a mixture of a Hartree-Fock exchange with DFT exchange correlation. Originally the exchange functional B includes the Slater exchange along with corrections involving the gradient of the density and the correlation functional LYP is that of Lee, Yang and Parr, which includes both local and non-local terms. The B3LYP functional is an approximation to the true exchange functional, which has shown to give a good description of interactions involved in the adsorption processes [10].

The adsorption energy $E_{ads.}$ of an adatom on the surface was calculated from the relation

$$E_{adsorption} = E_{complex} - E_{adsorbate} - E_{substrate} \qquad (1)$$

The terms appearing on the right hand side are the total energies of the complex (adsorbate + substrate), the adsorbate and the substrate, obtained from three independent calculations using the same supercell. The negative adsorption energy Eadsorption indicates that the bound adsorbate is electronically stable.

The Stevens, Basch and Krauss effective core potential triple zeta basis set CEP-121G was employed in the calculations. For a defect free cluster such as K_9Cl_{11} with 88 interacting electrons, there are 204 basis functions and 320 primitive gaussians. The computations were carried out using Gaussian 98-system [11].

Table 2: The total electronic energies E_{total} of the linear and non linear orientations of Z_1 centers at the surfaces of LiCl, NaCl and KCl. The total electronic energy differences ΔE_{total} (relative stabilities) are given in the last column. E_{total} are given in Hartrees and ΔE_{total} in eV.

	Dopant	Etotal linear	bent	ΔE_{total}
LiCl	Be^{2-}	**-177.0797617**	-177.0767756	0.081
	Mg^{2-}	-176.9332526	**-176.9343011**	0.029
	Ca^{2+}	-176.7816356	**-176.7890138**	0.200
NaCl	Be^{2-}	-173.5043125	-173.5030715	0.034
	Mg^{2-}	-173.3610761	**-173.3627482**	0.046
	Ca^{2-}	-173.2641167	**-173.2648744**	0.021
KCl	Be^{2-}	**-171.0951697**	-171.0925097	0.072
	Mg^{2-}	-170.9094016	**-170.9593499**	1.359
	Ca^{2-}	-170.8649421	**-170.8663421**	0.038

## 3. Results and Discussion

3.1 Z_1 center orientations
3.1.1 Relative stabilities

We start discussing our results by considering the relative stabilities of Z1 center orientations at the surfaces of LiCl, NaCl and KCl crystals. The two possible orientations of Z_1 center according to Bushnell, Stoenham and Luty [3] are shown in Fig.2. As shown in this Figure, the only difference between the two isomeric orientations is the site occupied by the divalent impurity I. The four basic constituents of Z1 are therefore I, Cl⁻, V⁻ and F center (V⁻ is the cation vacancy and F center is a single electron trapped in a nearest neighbor anion vacancy).

The calculated total electronic energies of the two orientations are given in Table 2. As one can see from this table, while the linear orientations of Be^{2+} doped surfaces were more stable than the non linear orientations by ca. 0.034-0.081 eV, the non linear orientations of Mg^{2+} and Ca^{2+} doped surfaces were more stable than the linear orientations by ca. 0.020-1.36 eV. The small energy differences between the linear and non linear orientations of Z_1 center could be one reason why the nature of most Z_1 centers is still unceratin. In the present cases, one might think of the center as an F center strongly perturbed by a neigboring positive ion vacancy and almost independent of the divalent positive ion position. Moreover, the relative stabilities of the linear and non linear orientations were neither dependent on the divalent cation impurity nor the monovalent host cation.

Table 3: The energy changes ΔE attributed to the simultaneous outward displacements of the nearest neighbor ions to the defectsites at LiCl, NaCl and KCl surfaces by 5% of the lattice parameter. Energies are given in eV.

Crystal	Dopant	ΔE
LiCl	Be^{2+}	1.76
	Mg^{2+}	1.50
	Ca^{2+}	2.53
NaCl	Be^{2+}	2.54
	Mg^{2+}	2.48
	Ca^{2+}	1.80
KCl	Be^{2+}	2.18
	Mg^{2+}	2.23
	Ca^{2+}	1.86

121
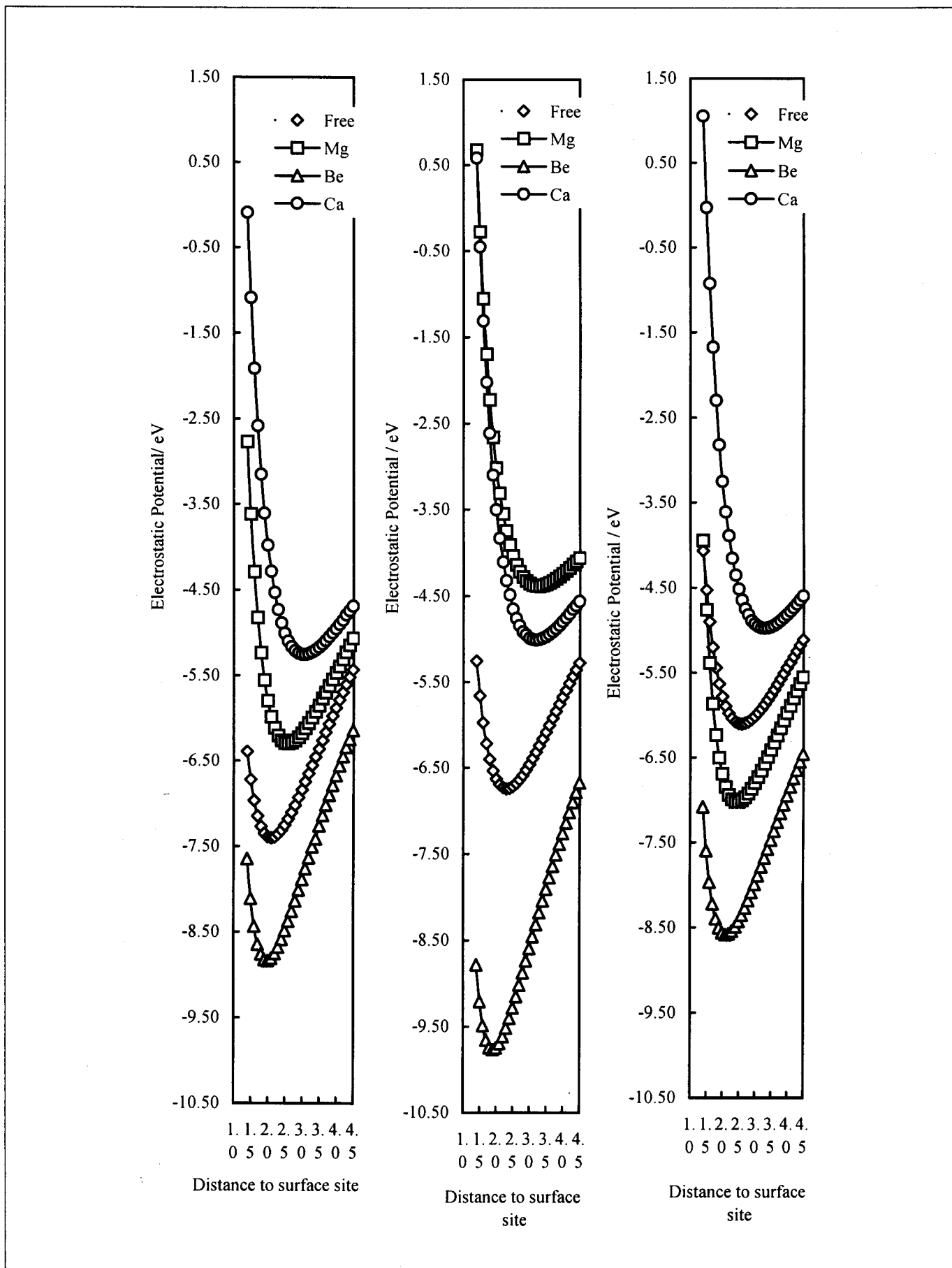
Figure 3: The electrostatic potential curves over the defeat free and defeat containing surfaces of LIcL, NaCl and KCl.

3.1.2 Relaxation effects

A complete treatment of lattice relaxation – in particular for Z_1 center – is a lengthy problem. Firstly, the ionic displacements around the defect sites (the divalent impurity, the cation vacancy and the neighboring F center) are not confined to the nearest neighbors and secondly, they are not totally symmetric. Moreover, several calculations give small relaxations of the surface layers, in agreement with low energy electron diffraction (LEED) experiments [12].

However, Z_1 center is likely to be associated with local distortions around the divalent impurity, the cation vacancy V^- and F center. We have therefore made an attempt to test how this will affect the total electronic energies of the relatively stable orientations. Firstly, we determined the optimal relaxation mode of the nearest neighbor ions to the defect sites. The optimal relaxation mode may be defined as the pattern of ionic displacements around the defect sites that lead to the largest total electronic energy lowering. This was found to be the outward displacements of all nearest neighbor ions to the defect sites. Secondly, the ions immediately surrounding the Z1 center were simultaneously displaced outward by 5 % of the lattice constant to estimate the contribution to the total electronic energy lowering. As shown in Table 3, the 5% displacements were found to lower the total electronic energies of B2+, Mg2+ and Ca2+ doped LiCl, NaCl and KCl surfaces by ca. 1.50 – 2.54 eV.

3.2 Z_1 center and interaction of atomic halogen
3.2.1 The surface electrostatic potentials

The electrostatic fields near the surface of an ionic crystal are so large and nonuniform [13]. We have therefore made an attempt to shed light on the expected electrostatic contributions to adsorbate-substrate inteactions under the effect of Z_1 center imperfection. We calculated the electrostatic potential curves over the monovalent cation site of the defect free surface and the divalent impurity site (Be^{2+}, Mg^{2+} and Ca^{2+}) of the defect containing surface at the distances considered for adsorbate-substrate inetractions in Angstroms. The electrostatic potential curves are shown in Fig.3, from which we observe that the elctrostatic potentials over the monovalent cations of the defect free surfaces and the divalent impurity cations of the defect containing surfaces are quite different. This means that one may expect quite different electric fields and electric field derivatives under the effect of Z_1 imperfection. Since the electrostatic interaction of the adatom with the surface will mainly consist of electric field-induced dipole and electric field derivatives induced quadruple moments, we also expect that classical contributions to the adatom-surface interactions are quite different under the effect of Z_1 center imperfection.

3.2.2 The adsorbate-substrate interactions

We may now consider the adsorbate-substrate interaction by examining the adsorption characteristics of atomic halogens (F, Cl, Br, I and At) at the defect free and defect containing surfaces of LiCl, NaCl and KCl to gain an overall picture of the effects of Z_1 center on the energetics of surface halogenation. We limited our investigation of different adsorption sites to the four cases of on-top adsorption on monovalent cation of the defect free surface and the three divalent cation impurities of the defect containing surface. The divalent cation impurity site provides unique characterization of Z_1 centers at the surface of the given crystal. The M_9Cl_{11} and $IV F$-M_7Cl_{11} clusters representing the defect free and the defect containing surfaces as well as the adsorption sites, namely, the monovalent cations (Li^+, Na^+ and K^+) of the defect free sur-
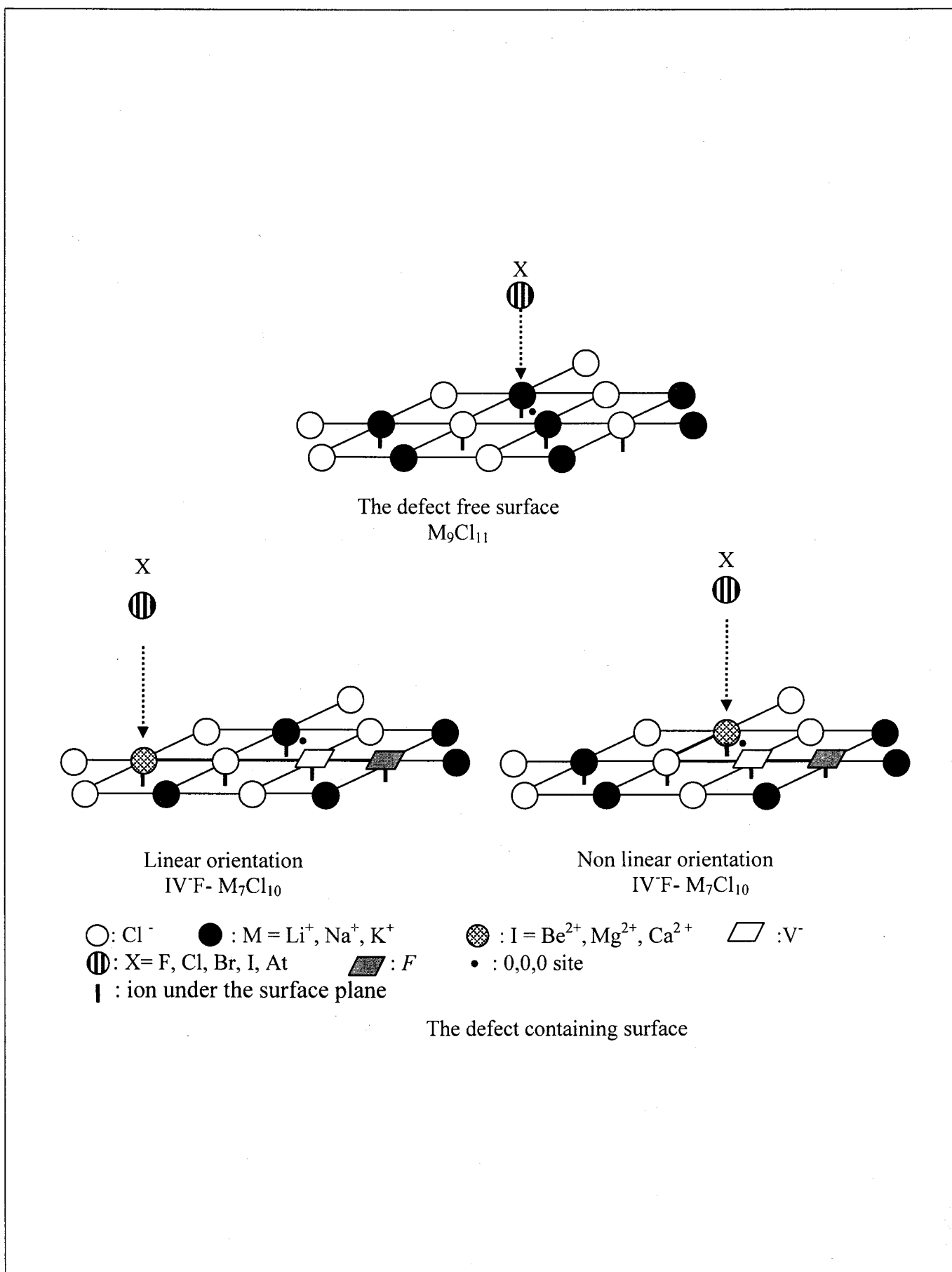
Figure 4: The adsorbtion of F, Cl, Br, I and At over the defect – free and defect containing of LiCl, NaCl and KCl.

faces and the divalent cation impurities (Be^{2+} for the linear orientation, and Mg^{2+} and Ca^{2+} for the non linear orientation) of the defect containing surfaces are shown in Fig.4, and the data for optimal adsorbate-substrate distances and optimal adsorption energies are given in Table 4. As shown in this Figure, the adsorption energy of the halogen atom over the defect free or defect containing surface is directly proportional to the electronegativity of the halogen. While the adsorption energy of the halogen atom was directly proportinal to the **charge density** of the monovalent cation of the defect free surface, it was independent on the **charge density** of the divalent cation impurity of the defect containing surface. The **charge density** is expected to increase with decreasing the screening effect of the inner shell electrons. The Z_1 center enhances the interaction between the incoming halogens and the considered adsorption sites drastically and changes the nature of surface **adsorption** from physical to chemical adsorption assuming a boundary value **between physisorption and chemisorption** of ca. 1.5 eV. Moreover, the calculated pattern of adorption energies is in consistence with the earlier expectations of electrostatic potentials curves, i.e, the calculated adsorption energies are quite different under the effect of Z1 center imperfeection.

3.2.3 The relative roles of energy gaps and spin pairing

To examine the relative roles of (i) the energy gap between the halogen atom and the substrate surface (ii) the spin pairing between the halogen atom single electron and the Z_1 single electron, in the course of the adsorbate substrate interactions, the tops of the valence bands and the bottoms of the conduction bands of the defect free surfaces, the highest occupied atomic orbitals HOAOs of the free halogens and the highest occupied molecular orbitals HOMOs of the defect containing surfaces have been calculated and repre-

Table 4: Data for optimal adsorption energies Eads/eV and adsorbate-substrate distances Re/Å of F, Cl, Br, I and At over the defect free and defect-containing surfaces of LiCl, NaCl and KCl.

	Dopant	F		Cl		Br		I		At	
		R_e	$E_{ads.}$	R_e	$E_{ads.}$	R_e	$E_{ads.}$	R_e	$E_{ads.}$	R_e	$E_{ads.}$
LiCl		1.93	-0.289	2.8	-0.086	3.1	-0.046	3.5	-0.0414	4.2	-0.041
	Be^{2-}	1.44	-6.20	2.0	-4.28	2.2	-3.67	2.47	-3.06	2.57	-2.77
	Mg^{2-}	1.86	-5.10	2.44	-4.01	2.62	-3.53	2.89	-3.17	2.98	-2.78
	Ca^{2-}	1.94	-5.07	2.74	-3.81	2.94	-3.36	3.23	-2.94	3.33	-2.69
NaCl		2.35	-0.185	3.03	-0.079	3.35	-0.047	3.68	-0.037	3.94	-0.040
	Be^{2-}	1.42	-6.15	1.93	-4.27	2.11	-3.66	2.35	-3.04	2.45	-2.75
	Mg^{2-}	1.84	-5.40	2.39	-4.29	2.54	-3.83	2.79	-3.37	2.9	-3.12
	Ca^{2-}	1.96	-5.10	2.73	-3.87	2.94	-3.43	3.21	-3.01	3.3	-2.76
KCl		2.6	-0.130	3.5	-0.077	3.81	-0.040	4.30	-0.035	4.33	-0.037
	Be^{2-}	1.4	-5.82	1.87	-4.01	2.03	-3.42	2.27	-2.82	2.36	-2.53
	Mg^{2-}	1.82	-5.07	2.35	-3.92	2.50	-3.46	2.74	-3.01	2.83	-2.77
	Ca^{2-}	1.95	-5.27	2.71	-4.01	2.91	-3.55	3.18	-3.14	3.27	-2.89

sented graphically in Fig.5. As shown in this Figure, the energy gap between the HOAO of free halogen and the top of the valence band of the closed shell defect free surface is always narrower than that between the HOAO of the same free halogen and the HOMO of the open shell defect containing surface. However, the free halogen adsorbs more strongly over the defect containing surface. We have therefore to conclud-estate that the spin pairing between the single electron of the incoming halogen and the Z_1 center single electron plays the dominant role-relative to the effect of the energy gap- in the course of the adsorbate-substrate interactions. This explanation might be applicable to all other open shell adsorbates over Z_1 center surfaces.

Table 5: The band gaps in eV of the defect free surfaces and the HOMO-LUMO of the defect containing surfaces of LiCl, NaCl and KCl.

Crystal	Dopant	⁻ E
LiCl		5.43
	Be2+	0.24
	Mg2+	0.35
	Ca2+	0.37
NaCl		4.86
	Be2+	0.38
	Mg2+	0.18
	Ca2+	0.25
KCl		4.39
	Be2+	1.55
	Mg2+	0.50
	Ca2+	0.22

3.2.4 Band gaps and electrical conductivity

To clarify the effect of Z_1 centers on the nature of LiCl, NaCl and KCl insulating surfaces, we have calculated the band gaps of the defect free and defect containing surfaces. The band gap was calculated as the difference between the top of the valence band and the bottom of the conduction band of the defect free surface, and the difference between HOMO and LUMO of the defect containing surface. These band gaps are collected in Table 5. The band gaps were calculated to be ca. 4.39-5.43 eV for the defect free surfaces and ca. 0.22-0.37 eV for the defect containing surfaces. The band gaps were therefore significantly reduced as a consequence of the valence and conduction band shifting and the insulating surfaces of the present alkali chlorides can be made semiconducting by Z1 center imperfection provided that the domain of band gaps of an insulating material to be ≥ 2 eV. Since the Z_1 center might be thought of as an F center strongly perturbed by a neigboring positive ion vacancy, we may attribute the semiconducting behavior of the Z_1 surface to the single electron of the F center.

Summary

An attempt has been made to examine the relative stabilities of Z_1 center orientations at the surfaces of Be^{2+}, Mg^{2+} and Ca^{2+} doped LiCl, NaCl and KCl ionic crystals as well as the effects of Z_1 center on the adsorption of atomic halogens (F, Cl, Br, I and At) using an embedded cluster model and density functional theory calculations.

While the linear orientations of the Be^{2+} doped surfaces were more stable than the non linear orientations, the non linear orientations of Mg^{2+} and Ca^{2+} doped surfaces were more stable than the linear orientations.

The relative stabilities were neither dependent on the type of the divalent cation impurity nor the type of the monovalent host cation. The Z_1 center changes the nature of atomic halogen adsorption from physical adsorption to chemical adsorption and the adsorption energies are directly proportional to the electronegativity of the halogen and the **charge density** of the host cation. The spin pairing mechanism plays the dominant role in the course of adsorbate-substrate interactions in addition to the **charge density**, and the surfaces can be made semiconducting by Z_1 center imperfection.

The detailed roles of spin pairing and charge density on the adsorption of Z_1 surfaces of other alkali halides is suggested for future examination.

REFERENCES

[1] **F.Agullo-Lopez, C.R.A. Catlow and P.D. Townsend,** *Point Defects in Materials*, Academic Press, London 1988.

K.M.Strohm and H.J.Paus, J.Phys. C: Solid State Phys.13 (1980) 57.

A.S.Shalabi, A.M.El-Mahdy, Kh.M.Eid and M.A.Kamel, Model. Simul. Mater. Eng. 7(1999) 1.

A.S.Shalabi, A.M.El-Nahas and A.A. Shalabi, J. Mol.. Model. 6 (2000) 26.

A.S.Shalabi, A.M.El-Mahdy and A.A.Shalabi, Current Applied Physics 1(2001)233.

[2] **A.S.Shalabi, A.M.El-Mahdy and A.A. Shalabi,** Physica B 305(2001)250.

[3] **J.C.Bushnell,** Thesis, Univ.of Illinois, unpublished (1964).

A.M.Stoneham, *Theory of Defects in Solids*, Oxford University Press, Oxford (1975).

J.H.Paus, Z.Phys.218 (1968) 57

F.Luty, Phys.Rev.Lett.20 (1968) 57

[4] **H.J.Freund and E.Umbach,** *Adsorption on Ordered Surfaces of Ionic Solids and Thin Films*, Springer, Berlin, (1993).

[5] **J.A.Horsley,** J.Am.Cerm.Soc. 101(1979) 2870.

K.H.Jhonson and S.V.Pepper, J.Appl.Phys. 53(1982) 6634.

A.B.Anderson, C.Ravimohan and S.P.Mehandru, Surf.Sci.183(1987) 438.

A.S.Shalabi, A.M.El-Mahdy, Kh.M.Eid, M.A.Kamel and A.A.El-Barbary, Surf.Sci. 488(2001)164.

[6] **A.S.Shalabi, A.M.El-Mahdy, M.A.Kamel and H.Y.Ammar,** Phys.B 292(2000)59.

A.S.Shalabi, A.M.El-Mahdy, M.A.Kamel and G.H.Ismail, J.Phys.and Chem. Solids 61(2000)1415.

[7] **A.S.Shalabi, A.M.El-Mahdy, M.A.Kamel and G.H.Ismail,** J.Phys. and Chem. Solids, 60(2001)1007.

A.S.Shalabi, A.M.El-Mahdy, M.A.Kamel and H.Y.Ammar, Phys.B 304(2001) 444.

[8] **A.S.Shalabi, M.E.Nour, A.M.Morsi and W.A.Zordoc,** Current Applied Physics 1 (2001) 427

A.S.Shalabi and A.M.El-Mahdy, J.Phys. and Chem.Solids, 60(1999)305.

A.S.Shalabi and A.M.El-Mahdy, Phys. Lett.A 281(2001)176.

[9] **A.D.Becke,** J.Chem.Phys. 98 (1993) 5648.

[10] **L.N.Kantorovich, J.M.holender and M.J.Gillan,** Surf.Sci., 343 (1995) 221.

L.N.Kantorovich and M.J.Gillan, Surf. Sci. 374 (1997) 373.

[11] **Gaussian 98,** Revision A.6, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M.A.Robb, J.R.Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E.Stratmann, J.C.Burant, S.Dapprich, J.M.Millam, A.D.Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B.Mennucci, C. Pomelli, C. Adamo, S.Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K.Malick, A.D.Rabuck, K. Raghavachari, J.B. Foresman, J.Cioslowski, J.V.Ortiz, B.B.Stefanov, G.Liu, A.Liashenko, P.Piskorz, I. Komaromi, R.Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L.Andres, C. Gonzalez, M. Head- Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

[12] **C.G.Kinniburgh,** J.Phys.,C9(1976)2695.

M.R.Welton-Cook and W.J.Bernardi, J.Phys.,15(1982)569.

T.Urano,T.Kanaji and M.Kaburagi, Surf.Sci.,134(1983)109.

P.A.Maksym, Surf.Sci., 149(1985)157.

D.L.Blanchard, D.L.Lessor, P.J.La- Femina, D.R.Baer, W.K.Ford and T.Guo, J.Vac.Sci.Technol., A9(1991)1814.

[13] **C.Z. Guo and L.W.Bruch** J.Chem.Phys. 97(1992) 7748.

A.Lakhlifi and C.Girardet, J.Chem.Phys.94 (1991) 688

R.Dovesi, R.Orlando, F.Ricca and C.Roetti, Surf.Sci.186 (1987) 267.

B.Deprick and A.Julg, Nouv. Chem.Phys.Lett.110 (1984) 150.

B.R.A. Nijboer, Physica, 125A(1984) 275.