The semiempirical approach to electronic structure of ionic crystal surface

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Abstract. Two essentially different semiempirical methods (Mulliken–Ruedenberg and INDO) have been used to calculate the electronic structure of the (001) surface for some alkali halides (LiF, LiCl, NaF, NaCl) within the framework of different surface models (slab infinite in two dimensions, molecular cluster and the slab placed over the point-ion support). The computational procedure has taken into account both the bond breaking of surface atoms and the electrostatic potential difference between the surface atoms and the bulk together with the charge density redistribution obtained self-consistently. The problem has been discussed of the optimum choice of the set of points in the two-dimensional Brillouin zone necessary for the calculation of the self-consistent crystal potential.

The molecular cluster model has been shown to be responsible for possible distortions of surface electronic states. The band structure calculations make evident the importance of bond-breaking effects of the surface ions even in the ionic crystals studied. The six-layer slab has been found to be large enough to reproduce both the surface states and the bulk states of a perfect crystal. The surfaces of fluorides have been found to possess a small positive charge whereas those of the chlorides are negatively charged, which causes a shift of the valence band top from the $\bar{\Gamma}$ point towards the $\bar{M}$ point. The influence of the number of layers in a slab is also studied. The results for the electronic structure of the surfaces of alkali halides are compared with those obtained by means of surface Green functions methods.

1. Introduction

The study of the electronic structure of perfect crystal surfaces is of great importance for the investigation of the chemisorption, catalysis, chemiluminescence, and kinetics of defect interaction on the surface, etc. The following three approaches are commonly used in the theoretical investigations of the electronic states of the surfaces of perfect ionic crystals.

(i) The electrostatic approach which takes into account only the differences between the crystal (Madelung) potential in a few layers near the surface and in the bulk (Levine and Mark 1966) and therefore describes only the so-called Tamm states. The model is able to make only qualitative predictions because it does not consider the change in coordination of surface ions and the redistribution of electronic density. The first effect has been supposed *a priori* to predominate in ionic crystals (e.g. in alkali halides).

(ii) The effect of dangling bonds on the surface atoms is taken into account in more

rigorous approaches based on the Green functions method and on the analytical continuation method (Zavt and Saks 1972, 1977, Saks and Zavt 1978, 1979, Levine and Davison 1970, Bennett 1974, Lee and Wong 1978). However, these methods also neglect the redistribution of electronic density in the layer near the surface, whose influence should be comparable with the effects in question themselves.

(iii) The quantum-chemical semiempirical methods generally are free from the mentioned shortcomings. However the choice of the model for the semi-infinite crystal affects the results in a way. The possible models are: the molecular cluster model (MC) (Satoko *et al* 1978, Kotomin *et al* 1980a, b) and the model which takes into account the periodicity in two directions of the crystal with a surface (Nishida 1978), in particular the large unit cell (LUC) model (Kotomin *et al* 1980b, Shluger 1981, Ermoshkin *et al* 1981). The latter model was presented and described by Evarestov (1975, see also Evarestov and Lovchikov 1977, 1979, Evarestov and Smirnov 1980, Harker and Larkins 1979).

Despite the fact that the *ab initio* approach has been recently used for studies of the surface of transition metals and light atoms, it is commonly known that the semiempirical approach is simpler than an *ab initio* one whereas calculations based on the latter are expensive and cumbersome. Besides, the semiempirical approach often yields better results than the *ab initio* approach since successfully derived parameters permit correlation effects to be taken into account and this approach is widely used now in the theory of both large molecules and crystals (Pople 1973, Pople and Beveridge 1970, Segal 1977). Moreover, the semiempirical approach has obvious advantages when calculating composite crystals with complex elementary cells, e.g. corundum (Evarestov *et al* 1980). It needs, in its turn, preliminary semiempirical studies of simpler binary crystals which are made in the present paper.

In the present paper a comparison is made of the results for a perfect (001) surface of a LiF crystal obtained by means of these two models. The calculations were made by two rather different semiempirical methods—the Mulliken–Ruedenberg (MR) method (Canadine and Hiller 1969) and the method of the intermediate neglect of the differential overlap (INDO) (Pople and Beveridge 1970). If the results obtained were found to be close to each other, it could argue for their independence on the concrete calculating scheme and the parameters used. Different methods for taking into account the influence of the bulk states on the surface electronic structure are investigated.

The band structure calculations (Ermoshkin and Evarestov 1978, Ermoshkin 1976, Evarestov *et al* 1980) for the alkali halides LiF, NaF, LiCl, and NaCl represent the electronic structure of thin films. Cooper and Bennett (1970) have shown that this permits us to investigate both the surface effects and the change in the electronic structure for films of varying thickness, both effects being of great interest[†]. Since there have so far been few experimental studies of ionic crystal surfaces (e.g. Sydor 1971), we believe our approach still has a predictive power here.

No direct and reliable experimental data concerning the rearrangement of the surface atoms in alkali halides are available. According to theoretical estimations this effect should be small and we have neglected it (cf Zavt and Saks 1972, 1977, Levine and Davison 1970, Bennett 1974, Tasker 1979).

[†] The semiempirical methods are known to reproduce inadequately the virtual states such as conduction band states in ionic crystals. Furthermore the valence s band states seem to be of minor interest in the problems of chemisorption, catalysis, etc. Therefore we discuss below only the upper valence p band.

2. Computational methods

A crystal infinite in two directions was studied by means of the MR and INDO methods in the framework of the LUC model. The band structure was calculated by the MR method (Ermoshkin 1976, Ermoshkin and Evarestov 1978). The parameters needed in the MR method were taken according to Ermoshkin *et al* (1975), the summation over the direct lattice included ions within five interatomic distances. The Hamiltonian matrix elements are given by

$$F_{\mu\nu}(k) = 0.5[2\varepsilon_\mu(q_M) + V_M^n + 2\varepsilon_\nu(q_N) + V_N^l] \sum_j \exp(ik \cdot R_j) S_{0\nu,j\mu}$$

$$+ 0.5(q_M + q_N) \sum_j \exp(ik \cdot R_j) S_{0\nu,j\mu}/r_{MN}$$

$$- \sum_j \exp(ik \cdot R_j) T_{0\nu,j\mu} - \delta_{MN}\delta_{\mu\nu}\varepsilon_\mu(q_M, n_M)$$

$$\mu \in M \qquad \nu \in N. \tag{2.1}$$

Here the indices $j\mu$ denote the element of μth atomic orbital on atom M from elementary cell j, R_j is a translation vector, $\varepsilon_\mu(q_M, n_M)$ is the ionisation potential of orbital μ on atom M with the atomic charge q_M and orbital population n_M, $S_{0\nu,j\mu}$ is the overlap integral, $T_{0\nu,j\mu}$ is the kinetic energy integral, and V_M^k is the Madelung energy at the site of atom M in layer k computed for a fixed electronic density distribution. The iteration procedure continues until self-consistent effective atomic charges q_M and electronic configuration $\{n_M\}$ are obtained. The charges q_M are calculated according to charge definition within the symmetrically orthogonalised basis of Löwdin (1950):

$$q_M = z_M^{\text{core}} - \sum_i^{M0} g_i \sum_\mu^M c_{i\mu}^* c_{i\mu} \qquad g_i = 0, 1, 2. \tag{2.2}$$

Here the orbital populations are equal to the diagonal elements of the crystal density matrix, which is calculated as a weighted sum over density matrices for some set of points in the Brillouin zone (BZ). The sets have been chosen according to the theory of special points (Chadi and Cohen 1973, Evarestov 1975, Evarestov and Smirnov 1980):

$$\rho(r) = \sum_{l=1}^t \alpha_l \sum_n |\psi_{nk_l}|^2, \qquad \sum_l \alpha_l = 1. \tag{2.3}$$

According to Chadi and Cohen (1973) there exists the following system of linear equations:

$$\sum_{l=1}^t \alpha_l \sum_{|R|=c_m} \exp(ik_l \cdot R) = 0 \qquad m = 1, 2, \dots, N. \tag{2.4}$$

Here $l = 1, 2, \dots, t$ stands for the set of chosen special points k_l in the BZ used instead of summation over all the k in the BZ. C_m is the distance to the mth neighbours, R is the direct lattice vector. The greater the m for which equation (2.4) holds, the more exact is expansion (2.3).

The crystal field potentials in different layers were computed taking into account the electronic density redistribution between the layers as well as (in the INDO) the difference in the anion and cation effective charges within each layer.

The Madelung potentials in the MR method read (in au):

$$V_M^1 = -1/R_{AB}(1.6155Q_1 + 0.068Q_2 - 0.002Q_3)$$

$$V_M^2 = -1/R_{AB}(1.6155Q_2 + 0.068(Q_1 + Q_3) - 0.002Q_{\text{perf}}) \qquad (2.5)$$

$$V_M^3 = -1/R_{AB}(1.6155Q_3 + 0.068(Q_2 + Q_{\text{perf}}) - 0.002(Q_1 + Q_{\text{perf}}))$$

where R_{AB} is the interatomic distance (half the lattice constant a_0), Q_i is the cation charge in the ith layer and Q_{perf} is the cation charge in the bulk.

The combination of the INDO method with the LUC model is a modification of the molecular INDO method by imposing periodical boundary conditions (cf Evarestov and Lovchikov 1977, 1979, Harker and Larkins 1979). So we can write for the Hamiltonian diagonal matrix elements in standard notation (Pople and Beveridge 1970) (off diagonal elements are identical to those given by Harker and Larkins (1979); see also Evarestov and Lovchikov (1977)):

$$F_{\mu\mu}^\alpha = U_{\mu\mu} + \sum_j \beta_A^0(S_{0\mu,j\mu} - \delta_{0j}) + \sum_\lambda^A [P_{\lambda\lambda}(\mu\mu|\lambda\lambda) - P_{\lambda\lambda}^\alpha(\mu\lambda|\mu\lambda)] + V_\mu$$

$$\lambda, \mu \in A_j, \qquad (2.6)$$

$$V_\mu = \sum_{C \neq A} \left(\sum_\sigma^C P_{\sigma\sigma}(\mu\mu|\sigma\sigma) - (z_C^{\text{nuc}}|\mu\mu) \right) + V_M^i - \sum_{C \neq A} \frac{Q_C}{R_C} \qquad (2.7)$$

$$Q_C = z_C^{\text{core}} - \sum_\lambda^C P_{\lambda\lambda}$$

where V_μ is the matrix element of the Madelung field on the μth atomic orbital on the atom A, taking into account the non-point nature of the surrounding ions within radius $R_M = \sqrt{48}R_{AB}$.

Due to rapid convergence, the lattice summation radii for the overlap and Coulomb integrals were chosen to be 11.7 au (three interatomic distances), whereas the exchange integrals were computed only for the nearest neighbours as suggested by Evarestov and Lovchikov (1979) (cf Harker and Larkins 1979).

The calculation and summation of the Coulomb integrals were done with an extended basis set including the anion and the cation σ *core* atomic orbitals (for details see Shluger *et al* 1980). Since the choice of parameters plays a vital role in semiempirical calculations, we employed preliminary calibration of the INDO parameters for reproducing the *experimental* band structure properties of a bulk LiF crystal (Shluger *et al* 1979, Shluger 1981, cf Nishida 1978). These parameters were also found to be capable of reproducing the properties of intrinsic defects—hole centres H, V_k, V_2 in LiF (Shluger and Kotomin 1981). The parameters obtained by the method have been fitted to the electronic features of the perfect LiF crystal according to Shluger *et al* 1979 (cf Nishida 1978). The parameters obtained are given in table 1.

Table 1. Parameters of the INDO method for a perfect LiF crystal.

	Atomic orbital	ξ (au^{-1})	β (eV)	E_{neg} (eV)
Li	2s	1.2	−4.5	−2.65
F	2s	1.95	−10.8	−23.24
	2p	1.75	−10.8	−4.1

The band structure calculations have been performed self-consistently; the crystal electronic density has been computed at each iteration by summation over special points in the reciprocal lattice chosen according to the theory of special points in the Brillouin zone (BZ) (Chadi and Cohen 1973, Evarestov 1975). The BZ for a two-dimensional square lattice is given in figure 1. The LUC model is meant to compute the electronic density and one-electron energies only at a few BZ points (usually at symmetry points) whereas the computer program for band structure calculations (Ermoshkin *et al* 1980)
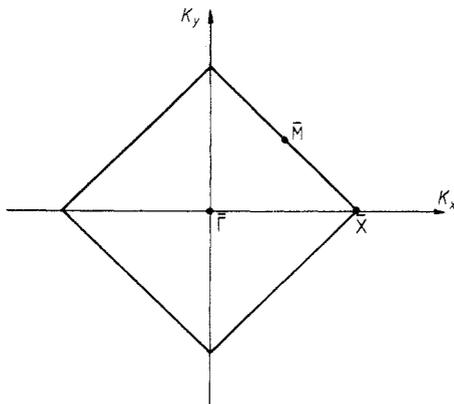

Figure 1. The two-dimensional Brillouin zone for the square lattice.

permits us to calculate these quantities at *any* point in the BZ. Effective charge of atoms obtained self-consistently for some set of special points by means of the LUC model could be used then for the band-structure calculations in computing one-electron energies along the directions of interest in the BZ. We have proceeded in such a manner in the calculations of three-layer slab surface models.

3. The models of a crystal surface

Some points should be made before we discuss the models of the (001) surface of ionic crystals used in the present calculations.

(i) The LUC model which makes use of periodical boundary conditions appears to be preferable to the MC model, because it reproduces correctly the transitional symmetry of the crystal with the surface. However, it should be noted that in studying chemisorption and the role of the slab thickness, the use of the LUC model involves enormous computational difficulties. This necessitates a comparison of the results obtained by means of two models in order to clarify the possibilities of the MC model and the electronic structure distortions which it causes.

(ii) The available computations of the surface electronic structure of alkali halides do not allow us to draw definite conclusions about the relation between the 'Madelung' effect and the effect of bond breaking at the surface†.

† These effects determine the so-called Tamm and Shockley surface states respectively.

(iii) The manner and degree in which the crystal surface affects the electronic struc-
ture of deeper layers still remain obscure. From this point of view it seems to be important
to clarify the connection between the form of the dispersion curves and the electronic
localisation (i.e. the participation in the crystal orbitals of atomic orbitals from atoms in
different layers). It is known that the Madelung potential in the third layer below the
(001) surface is almost equal to the bulk one (e.g. Kassim and Matthew 1977). However,
it is not clear *a priori* how deep the influence of bond breaking and the electron density
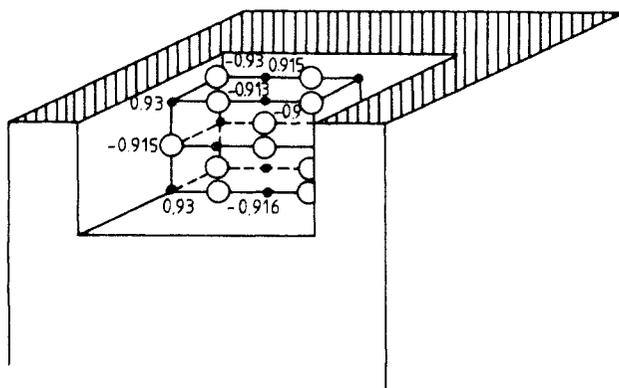redistribution caused by the surface spreads.

Figure 2. The molecular cluster simulating a LiF (001) surface. The effective charges of ions
are given (symmetrically equivalent ions have equal charges).

(iv) Since the translation of the unit cell along two directions parallel to the surface
creates a crystal of a slab form with *finite* thickness, examination of the connection
between the electronic properties and the number of layers is of great importance.

Proceeding from these considerations we have undertaken the calculations employ-
ing two models. (i) The three-layer MC model (figure 2) and the slab model, consisting
of three layers which are infinite in two dimensions. These layers are placed over the
semi-infinite crystal whose influence is restricted only to the electrostatic field. (The MC
is surrounded by the semi-infinite crystal from all faces except for the surface-simulating
one.) The charges on the atoms of a support are chosen equal to those in bulk and the
crystal potential in the three layers is taken according to equation (2.7) (cf Kotomin *et
al* 1980a, b). If the Madelung effect were predominant, one should expect this model to
describe the one-electron surface states correctly. (ii) A thick slab consisting of n layers
($n = 3$–8). Here the edge layers simulate the surface whereas the middle layers are
expected to reproduce the bulk in the case of sufficient slab thickness.

The calculations in the framework of the first model are performed using the MC
$(Li_4F_4)_3$ (figure 2) and the LUC $(A_4B_4)_3$. The latter is obtained by twofold expansion of
the primitive unit cell $(AB)_3$ along two directions ($\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$). Such a LUC has
translational vectors $a_0\{110\}$ and $a_0\{1\bar{1}0\}$ (a_0 is the lattice constant) and reproduces the
electronic states at points $\bar{\Gamma}$, $\bar{X}$ and $\bar{M}$ of the two-dimensional BZ (figure 1).

Calculations which make use of the second model would require great LUC's for a
reasonable number of layers (exceeding 140 basis functions). It is stated in § 5 that the
usual band structure calculation appears to be much more efficient here than the cor-

responding calculation in the framework of the LUC model since the evaluation of a self-consistent crystalline potential requires the solution of a secular equation for the unit cell $(AB)_n$ only in three different points of the irreducible part of the BZ (corresponding to nine points in the whole BZ).

4. Comparison of calculation of the LiF surface states by the MC and the LUC models

We discuss here the calculation results obtained by means of the first model (using LiF as an example). The cluster calculations were performed by the INDO method and the

Table 2. Effective charges (au) and crystal field matrix elements (eV) for three layers near a LiF (001) surface obtained by the INDO method. Note that the bulk $|q|$ value is equal to 0.88 and 0.75 for the MC and the LUC respectively. The experimental estimate is 0.82 (Batzanov 1975). The difference between potentials for cationic and anionic sites is due to the non-point-ion effects considered (cf Shluger *et al* 1979). Effective charges q_K, q_A are given for ions with maximal number of nearest neighbours.

Model	q_K	q_A	V_K	V_A
	0.915	−0.913	7.84	−11.02
MC	0.899	−0.901	7.51	−11.35
	0.916	−0.916	7.67	−11.46
	0.788	−0.783	6.10	−9.41
LUC	0.754	−0.759	5.63	−9.55
	0.788	−0.788	5.99	−9.71

LUC calculations were made within both the INDO and the MR schemes. In order to compare the results of different calculations it is expedient to distinguish the following main features: (i) the effective charges $q_{K,A}$ on cations and anions in different layers; (ii) the participation of atomic orbitals from ions in different layers in the valence-band crystal orbitals (according to a simple electrostatic model (Levine and Mark 1966), the electronic states split off the top of valence band should be connected mainly with the surface atomic orbitals; (iii) the crystal potentials at ionic and cationic sites in different layers.

Figure 2 shows the effective charges obtained for the MC placed over the support. It can be seen that the cations (anions) within each layer have different charges due to their non-equivalence (different number of neighbours). The charges on the ions in the cluster models of perfect crystals behave in a similar way (e.g. Ermoshkin *et al* 1975, Ermoshkin 1976, Kotomin *et al* 1980b) and this is connected with the inadequacy of the point-charge approximation of broken bonds between the MC and the host crystal.

The one-electron states at the top of the valence band are connected essentially ($\geqslant 70\%$) with the orbitals of the surface ions and the sequence of states follows the change in the crystal potential of surface layers† (see table 2 and full curves in figure 3(*a*)). Here and below, the states containing more than 70% of the edge atom atomic orbitals should be considered as surface ones.

The values of $q_{K,A}$ obtained for ions within the LUC model are also given in table 2. It can be seen that these charges are significantly smaller than the mean values of those

† Similar results have also been obtained for MC in NaCl having other form (Kotomin *et al* 1980b).

in the MC model. A lowering of atomic charges obtained in the LUC model has also been reported in other papers (e.g. Harker and Larkins 1979), and this is possibly due to a greater number of interacting ions being considered. The results of the MC method exhibit similar charge values (see below). Both in the MC and the LUC models, the $q_{K,A}$ of the surface atoms are smaller than those in the bulk.
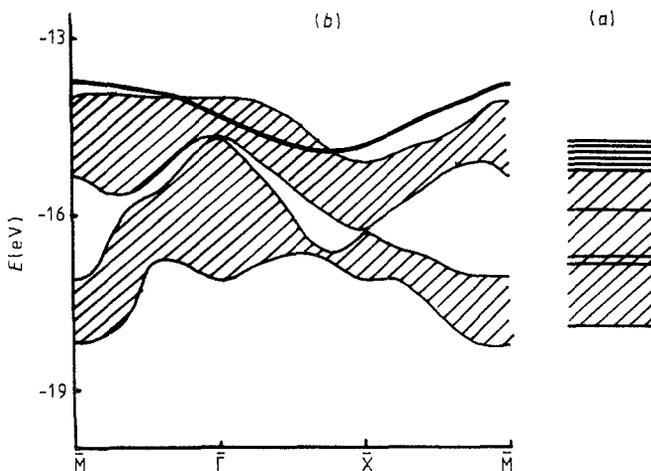

Figure 3. (*a*) The electronic structure of LiF (001) surface obtained within the MC model (figure 2) by the INDO method. (*b*) The band structure of LiF (001) surface simulated by three layers placed above the point-ion support. The full curve corresponds to the states containing more than 70% of surface ion orbitals.

In the LUC model the charges of similar ions in the layer are identical (compare with MC). At the same time cations and anions in the same layer have slightly different charges (both in the MC and in the LUC models) (cf Kotomin *et al* 1980a, b). Unlike the MC calculations, the structure of the surface states does not correlate directly with the change in the crystal potential, which, however, demonstrates a behaviour similar to that in the cluster model (table 2). In our opinion it results from relatively smaller changes in the potential for different layers near the surface, due to smaller charges on atoms obtained in the LUC model. The crystal orbitals of states near the top of the valence band, computed in the LUC model by means of both MR and INDO schemes, contain orbitals of ions from the first and the third layers with *close* weights. This is evidently caused by comparable effects of a substantial change in the resonance integrals for the ions in layers I and III (these integrals are identical due to the bond breaking) as compared with that in layer II and the change in the electrostatic potential within these layers. This is confirmed by the fact that the bands connected with p_z atomic orbitals of layers I and III, which have the largest change in the resonance integral (since the z axis is perpendicular to a crystal surface), appear near the *middle* of the valence band.

In figure 3(*b*) the results are given of band structure calculation by means of the MR method for an LiF (001) surface simulated by three layers on the support. A self-consistent crystal potential is obtained by the LUC $(Li_4F_4)_3$. A significant split of surface states off the valence band (VB) can be observed. However, the contribution of orbitals from atoms in the first layer in the states near the top of VB (at the $\bar{\Gamma}$ point) does not exceed 50%. This is connected with a large participation of atoms from the third layer

and is due to the comparable importance of both effects: the bond breaking and the electrostatic one in the third layer. Note that the INDO scheme, contrary to the MR method, takes into account the difference in crystal potentials for $p_{x,y}$ and p_z atomic orbitals. The crystal potentials for p_z atomic orbitals on the surface atoms exceed those for $p_{x,y}$ aromic orbitals by about 0.3 eV only, which does not influence the results noticeably.

Similar results have also been obtained in the band structure calculations by the MR method for other ionic crystals—LiCl, NaF and NaCl. In these calculations the top of the VB (including the surface states) appears to be shifted towards the $\bar{M}$ point (the top of the bulk VB in alkali halides, as is well known, is the Γ point).

The main conclusion of this section is that a small cluster may significantly distort the electronic structure of a semi-infinite crystal. This is connected with dispersion of the values of the obtained effective charges (which causes an error in the Madelung energies) as well as with a great number of cluster-broken bonds.

It is well known (Zavt and Saks 1972, 1977, Saks and Zavt 1978, 1979, Levine and Davison 1970, Bennett 1974, Cooper and Bennett 1970) that the appearance of surface states largely depends on the choice of parameters employed. Therefore it should be emphasised that the accuracy of our results is supported by the evaluation of identical results by means of two quite different methods and sets of parameters. Unlike the conventional MC model, the crystal fields at the sites of anions (cations) in the layer are identical within our scheme (Shluger *et al* 1979), which enables us to investigate the 'pure' surface bond-breaking effect.

5. Calculation of thin films

In the above-described band structure calculations for a three-layer slab by means of the MR method, the self-consistent potentials were taken from the LUC calculations. However, the LUC model appears to be cumbersome and unrealistic for a greater number of layers. That is why we are undertaking a study of the effect of the choice of a set of special points in the BZ on the features of a crystal (thin film) restricted by a surface calculated in the framework of the band structure scheme (equation (2.1)).

The optimum choice of a set of special points has been evaluated by comparison of different sets (see table 3). The last column contains the number of terms m for which equation (2.4) holds. The greater the number of points in a k space, the better is the electronic density approximation. The increase of the number of points in a set from 4 to 8 causes a change in $|q|$ of about 0.03 e; from 8 to 9, about 0.004 e; from 4 to 16, about 0.006 e; and from 8 to 25, about 0.005 e. So the set of nine special points corresponds to a saturation of results and appears to be quite satisfactory. Therefore the calculations below of thin film bands were performed using a self-consistent charge obtained for a given set of nine special points. The one-electron energies in turn were computed with this crystal potential at more than 100 points in the BZ.

The band structure has been calculated for LiF, NaF, LiCl, and NaCl crystals. We are now discussing the electronic structure for a six-layer slab of NaCl crystal (as an example). Figure 4 shows the corresponding dispersion curves and the electronic density of states (DOS) curve. The full curves within the shaded region depict the electronic band states localised to more than 70% on the surface atoms† (here the surface is simulated

† In these states the contribution of atomic orbitals from other layers decreases with the layer depth, which is characteristic of surface states.

Table 3. Different sets of special points used in the electronic density distribution computations.

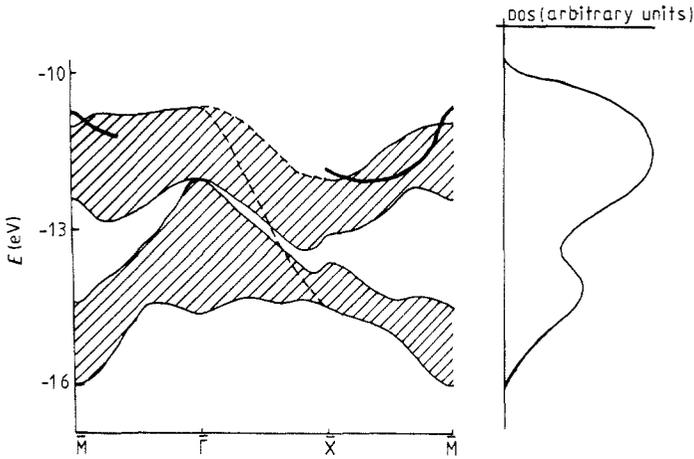| Number of points in BZ	Stars of points $(2\pi/a_0)$	Weights of points	Number of terms for which (2.4) holds
4	$\bar{\Gamma}(0,0)$; $\bar{X}(1,0)$; $\bar{M}(\frac{1}{2},\frac{1}{2})$	1, 2, 1	2
8	$\bar{\Gamma}$; $\bar{X}$; $\bar{M}$; $(0,\frac{1}{2})$	1, 1, 2, 4	4
9	$\bar{\Gamma}$; $(0,\frac{2}{3})$; $(\frac{1}{3},\frac{1}{3})$	1, 4, 4	5
16	$\bar{\Gamma}$; $\bar{X}$; $\bar{M}$; $(\frac{1}{4},\frac{1}{4})$; $(0,\frac{1}{2})$; $(\frac{1}{4},\frac{3}{4})$	1, 1, 2, 4, 4, 4	8
25	$\bar{\Gamma}$; $(\frac{2}{10},\frac{2}{10})$; $(\frac{4}{10},0)$; $(\frac{4}{10},\frac{4}{10})$; $(\frac{2}{5},\frac{1}{5})$; $(\frac{4}{5},0)$	1, 4, 4, 4, 8, 4	12

Figure 4. The band structure of a six-layer NaCl slab. The broken curve reproduces the quasi-bulk dispersion curve. The right-hand scale contains the DOS curve.

Table 4. The effective charges of ions (in au) for NaCl slabs of different thicknesses. $|q|$ (bulk) = 0.6313; the experimental value is 0.74 (Batzanov 1975).

Number of layers	Layer number							
	1	2	3	4	5	6	7	8
3	0.618	0.652	0.666					
	−0.620	−0.648	−0.668					
5	0.623	0.631	0.632	0.631	0.623			
	−0.625	−0.630	−0.632	−0.630	−0.625			
8	0.623	0.631	0.632	0.632	0.632	0.632	0.631	0.623
	−0.624	−0.630	−0.632	−0.632	−0.632	−0.632	−0.630	−0.624

by *two* (I and III) layers). In our calculations a split-off of surface states up to 0.2 eV into the gap may be observed near the $\bar{M}$ and $\bar{X}$ points. The states connected predominantly with p_x and p_y atomic orbitals of the surface atoms appear near the top of the VB, whereas the p_z atomic orbitals are located in the middle of the VB as mentioned above. Within the VB states there appear discontinuities or lagoons (independent of the number of layers) which have been obtained before by the Green function method (Zavt and Saks 1977, Saks and Zavt 1978, Saks 1979).

The same figure also depicts the dispersion curves (along the $\bar{\Gamma}$–$\bar{X}$ direction) corresponding to two middle layer atoms, which simulate the bulk†. These bands are very similar to those for the bulk. Such bands for five-, six, and eight-layer slabs are qualitatively similar. The effective charge on cations and anions from different layers for three-, five-, six- and eight-layer slabs are given in table 4. An increase of slab thickness from three to five layers still noticeably changes the effective charges. Further increase does not affect the results significantly and the ion charges in the middle layer are very close to those for the bulk obtained in similar calculation.

Figure 4 also depicts the DOS curve which was obtained by means of a smoothing procedure, using the Lorentz rule for broadening a single level:

$$N(E) = \sum_i \frac{w_i \sigma}{\pi} \frac{1}{(E - E_i)^2 + \sigma^2}. \tag{5.1}$$

Here σ is the broadening factor which was chosen equal to 0.5 eV to reproduce the experimental halfwidth for bulk VB, w_i is the weighting factor, i.e. the number of the symmetry equivalent points in the BZ.

Comparison of the DOS curves for bulk and slab shows that the peak of the curve for the slab DOS is situated 0.4 eV higher than that for the bulk DOS. It is also broadened, compared with the bulk DOS, to the lower-energy side, which is due to participation of surface states shown above in the band structure. The appearance of the second (lower) maximum is connected with the presence, near the VB bottom, of a significant number of electronic states with an essential ($\simeq 50\%$) admixture of surface atomic orbitals (see also Ermoshkin *et al* 1981).

We have used the six-layer slab model in other surface calculations since we have found that it reproduces the main trends quite adequately.

The band structure for an LiCl crystal (figure 5) is quite analogous to that for NaCl. Figure 6 shows the band structure for an LiF crystal (cf. similarity with figure 3(*b*)). The main distinction from NaCl is that the surface states arise over *all* the BZ directions studied but only near the $\bar{M}$ and $\bar{X}$ points are these states split off into the gap from the continuum. Quite analogous is the situation for the NaF crystal (figure 7) except for the appearance of the surface states within the gap, also in the $\bar{\Gamma}$ point. Similarity of the band structure of two chlorides (fluorides) proves the reliability of the results obtained.

It can be seen from table 5 that the surface layers in fluorides are positively charged whereas for chlorides they are negatively charged. This effect is rather small but it is reliably observed for all four crystals and for slabs of varying thickness. In particular, the decreasing number of layers is accompanied by an increase in the surface charge, which might be experimentally determined for very thin films. The surface layer charge causes a slight band bending (the $\bar{\Gamma}$ point in fluoride bands is situated slightly below the $\bar{M}$ point).

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† The $\bar{\Gamma}$–$\bar{X}$ direction has been chosen to have a full analogy to the same direction in the BZ for a bulk FCC crystal. The $\bar{M}$ and $\bar{L}$ points of two-dimensional and three-dimensional BZ can be compared, the former being the projection of the latter onto the $z = 0$ plane (Cracknell 1976).
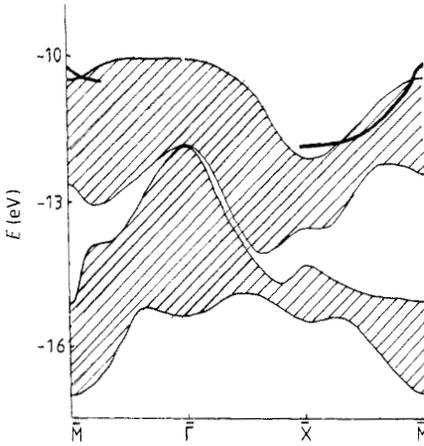
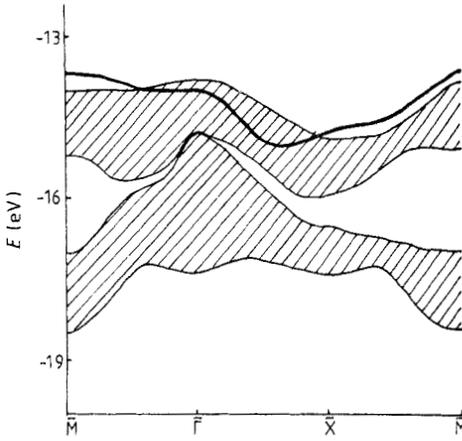**Figure 5.** Energy bands for LiCl crystal. Notations similar to those for figure 4.

Figure 6. Energy bands for a LiF crystal (cf. figure 3(b)). Notations are the same as for figure 4.
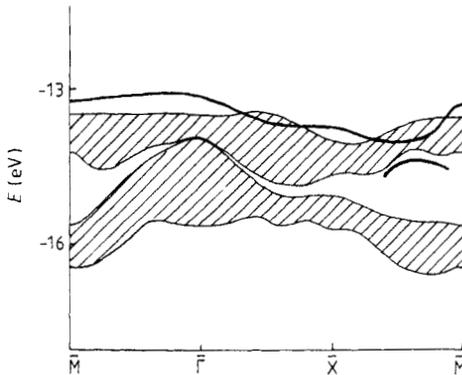

Figure 7. Energy bands for a NaF crystal. Notations are the same as for figure 4.

The calculations of films of different thickness show that the VB width, E_p^w, (including the surface states) for a three-layer slab is less than that for the bulk. It becomes larger than the bulk VB width for a six-layer slab and does not significantly change for a thicker slab. For example, the VB width for a bulk NaCl is equal to 5.09 eV, whereas the VB widths for three-, six-, and eight-layer slabs are equal to 5.05, 5.40, and ≥5.44 eV respectively.

Table 5. The layer charges for LiF, LiCl, NaF and NaCl crystals obtained for a six-layer slab.

Species	Layer number					
	1	2	3	4	5	6
LiF	0.003	−0.002	−0.002	−0.002	−0.002	0.003
LiCl	−0.001	0.001	0	0	0.001	−0.001
NaF	0.002	−0.001	−0.001	−0.001	−0.001	0.002
NaCl	−0.001	0.001	0	0	0.001	−0.001

Thus the simulation of the (001) surface of ionic crystals by a six-layer slab already permits us to obtain the main features of crystal electronic structure both bulk and surface.

6. Conclusion and discussion

Comparison of results obtained in § 5 for chlorides with those for calculating the KCl surface states by the Green functions method (Zavt and Saks 1972, Saks and Zavt 1978, Saks 1979) confirms the earlier consideration about the sensitivity of the split-off of surface electronic states value to the two main factors determining this effect: namely, the change of the electronic field near the surface and the bond breaking. In papers by Zavt and Saks (1972, 1977) and Saks and Zavt (1978) and in the present paper both effects have been taken into account. However the use in the papers by Zavt and Saks of parameters by De Cicco (1967) which are responsible for an unrealistically narrow VB of a perfect KCl crystal ($\simeq 0.8$ eV), the use of overestimated ionic charge (± 1) as well as the neglect of the electronic density redistribution in calculating the electrostatic field should account for the difference from our results in the split-off values of surface states in different BZ points.

In particular, Zavt and Saks (1972, 1977) and Saks and Zavt (1978) observed a split-off valence band at the $\bar{\Gamma}$ point in KCl, which contradicts our calculations of chlorides. It should be stressed that our *definition* of the surface state (i.e. ≥70% of surface atomic orbitals) is rather rigid. Simultaneously 'softening' of this condition (down to 50%) and taking into account the contribution of the *second* layer should permit us, e.g. to classify also the top of the VB at the $\bar{\Gamma}$ point of NaCl as a split-off.

On the other hand, the split-off of the valence band may be stated in our slab model *only* within an accuracy of a separation between the energy levels simulating the VB (≤0.1 eV for six-layer slab).

It should be stressed however that the split-off values in *both* calculations are of the order of 0.1–0.2 eV, which makes their experimental verification rather complicated. In

both calculations there appear lagoons within the VB and surface states within the continuum energy spectrum. (Note that Zavt and Saks (1977) employed another BZ points classification).

The above-mentioned sensitivity of the results to the two effects is in agreement with the conclusions of Lee *et al* (1978), where the split-off of the Tamm states in MgO were obtained only for values of the first effect larger than some critical value.

The self-consistent approach to the crystal surface effects in our calculation as well as the independence of the results obtained from the choice of the computational procedure (the MR or the INDO) and from the model used (MC and LUC placed on a support or slabs of different thicknesses—three, five, six or eight layers) allow us to confidently draw the following conclusions.

(i) Despite the fact that a small molecular cluster may distort the electronic structure (and $q_{K,A}$) of a semi-infinite crystal, perhaps this model might be successfully applied to chemisorption processes due to the local character of the interaction. Direct comparison of MC and LUC calculations is impossible due to the absence of a BZ concept for the former model.

(ii) The surface electronic states are greatly affected by the bond breaking of surface atoms even in the ionic crystals. Therefore, an efficient consideration of the charge density distribution in the bulk, and, particularly, of the surface charge distribution, is needed. The neglect of the former may overestimate the difference between the bulk and the surface electrostatic field, which would further add to the incorrectness of the surface dispersion curves. A consideration of the latter effect, in turn, enables us to investigate such delicate properties as the surface charge and band bending. The changes in the charges of the surface ions being small, the bulk parameters were used in surface calculations, and this means neglect of the surface ion polarisation due to an electric field gradient.

(iii) As has been concluded by Shluger *et al* (1979), the conventional calculation of the INDO–LUC scheme (Evarestov and Lovchikov 1977, 1979, Harker and Larkins 1979) *fails* to provide the right nature of the surface states of the ionic crystals due to an incorrect way of calculating the crystalline field near the surface.

(iv) The application of a slab model to an ionic crystal surface appears to be successful. The limited number of layers (about six) has proved to be sufficient to reproduce the bulk and the surface electronic structure.

(v) In order to obtain a self-consistent distribution of electronic density in the band structure calculations performed a set of nine special points in the BZ (cf table 3) has been found to be satisfactory.

Despite the fact that the consequences of the approximations involved in our semi-empirical calculations could not be examined in detail, the reliability of our results is confirmed by the fact that two essentially different methods used—the INDO and MR—yield *close* results. Moreover, the comparison (when possible) of our results with those obtained by the surface Green functions method (§ 5) also reveals reasonable agreement. On the other hand, the semiempirical quantum-chemical methods permit one to easily take into account the effects connected with charge redistribution near the surface. Shluger (1981) and Ermoshkin *et al* (1981) have analysed these effects in detail (for the LiF crystal as an example) and have shown that (i) a 0.03 e increase of anion effective charge at the surface results in the growth of the splitting off the valence band, produced by these anions, by 0.45 eV due to change of one-centre Coulomb and exchange interactions; (ii) the corresponding increase of the matrix elements of the non-point crystal-

line field on surface anions results in the *lowering* of the surface states by 0.2 eV. Therefore, the total effect of charge redistribution near the surface is their increase by 0.25 eV. The latter is close to the maximal split-off obtained by the surface Green functions method (0.2 eV in KCl, Zavt and Saks 1977) and thus can play a vital role in surface calculations.

Acknowledgments

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