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Quantum-Chemical Calculations of Electronic and Hole Centres and Surface of NaCl Crystals (II)[2])

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Parameters of the CNDO method in a molecular cluster model derived in the first part of the paper are used for calculating the electronic structure of a number of defects in the ionic NaCl crystal. Hole (V_K, H) centres, the surface as a defect, the F centre on the surface and in the first layer below it are considered. The positions of one-electron defect levels within the gap of the perfect crystal are discussed. The models of the V_K, H centres as Cl_2^- and Cl_4^{3-} molecular ions in a crystal are confirmed. The results of the calculations based on the crystal field estimates (given in the first part of the paper) and the standard CNDO calculation scheme indicate that a more correct estimate of the electron interaction energy is necessary.

Параметры метода ППДП в модели молекулярного кластера, полученные в первой части работы, использованы при расчете электронной структуры ряда дефектов ионного кристалла NaCl. Рассмотрены дырочные (V_K,H) центры, поверхность как дефект, F центр на поверхности и в первом слое под ней. Обсуждается положение одноэлектронных уровней дефектов в запрещенной зоне совершенного кристалла. Подтверждены модели дырочных центров как Cl_2^- и Cl_4^{3-} молекулярных ионов в кристалле. Результаты расчетов, использующих метод оценки кристаллического поля (приведенный в первой части работы) и стандартную схему ППДП, свидетельствуют о необходимости более точного расчета межэлектронного взаимодействия.

1. Introduction

In the first part of the paper (hereafter referred to as I) a new parametrization scheme for calculating the electronic structure of defects by the CNDO semiempirical method in a molecular cluster (MC) approach has been presented and developed. This scheme also involves the calculation of the crystal field energy in a MC lattice site produced by non-point ions *outside* the MC (unlike the traditional point-ion model).

The idea of our scheme is to calibrate the parameters by calculating the distinctive features of a perfect crystal (first of all, the energy of the p valence band midpoint and its width). The parameters obtained are then employed for calculating the properties of a series of very different defects (both bulk and surface ones) relating the positions of their levels to the band scheme of a perfect crystal. Such an approach permits to take directly into account the crystalline nature of objects under investigation.

In I we have derived parameters of the NaCl crystal and have also shown that the properties of the bulk F centre are well reproduced only if an additional function (AF) centered at an anion vacancy is involved. Its parameters are presented.

In this part of the paper the CNDO calculations of the hole (V_K, H) centres, the "perfect" surface, and two kinds of the surface F centres are performed employing the parameters derived in I. We shall now follow consecutively the standard CNDO calculation scheme [1] in order to clarify its advantages and shortcomings.

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2. Hole Centres

The calculation of the electronic structure of two fundamental hole centres, V_K and H centres, is of great interest for two reasons. (i) Their local states originate from the valence band (unlike electronic centres) whose features are suitably described by the tight-binding method. (ii) To our knowledge there have so far been no theoretical papers in which the electronic structure of ions neighbouring the X_2^- quasi-molecule and the hole delocalization are taken into account and where their level positions are related to the band scheme of a perfect crystal.

2.1 V_K centre

Optical and spin resonance data on the V_K centres (the self-trapped holes) in halide lattices indicate features resembling those of a free molecular ion X_2^- and the latter is the generally accepted model of the V_K centre [2 to 4]. The only effect of a crystal in such a model of a "molecule in a crystal" is a change of the internuclear separation as compared to a free ion. Since absorption in both UV and IR bands produces a valence band hole, both the *excited* one-electron states σ_g, π_g evidently fall into the valence band.

We discarded the a priori hypothesis that a hole is entirely localized on the X_2^- molecule and simulated the V_K centre in the form of the MC shown in Fig. 1a. The MC is embedded in the crystal field of the rest crystal and the ion-size effect described in I, Section 2.2, is also taken into account.

Fig. 2 shows the corresponding one-electron levels calculated by the CNDO approximation of the unrestricted Hartree-Fock method and related to the perfect crystal
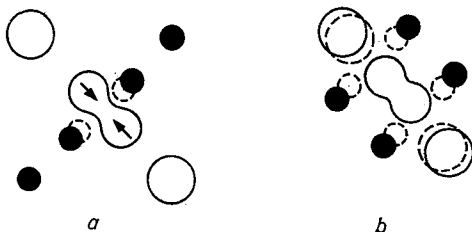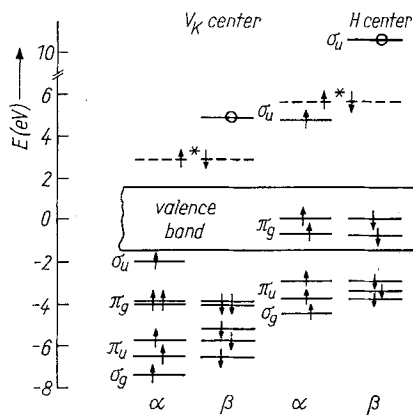

Fig. 1

Fig. 2

Fig. 1. Two molecular clusters simulating the (a) V_K and (b) H centres (schematically). The geometry is taken from [5]

Fig. 2. Positions of V_K and H centre levels within the gap (whose Hartree-Fock value is 8.6 + + 4.0 = 12.6 eV). The asterisk indicates the relaxed level occupied by an additional electron

band scheme. One can conclude that the patterns for α and β spin are rather different. For the β-spin pattern the *virtual* σ_u level, occupied by a hole, lies above the top of the valence band whereas the σ_g level lies above two π_u levels (the latter do not participate in optical transitions).

A similar pattern is also revealed for the free Cl_2^- molecule and this is likely due to the difference between the one-centre Coulomb and the exchange interaction terms, $(P_{AA} - P_{\mu\mu}^{\alpha(\beta)}) \gamma_{AA}$, ($|\mu\rangle$ is the AO making the main contribution to the σ_u state) for α and β spin which enter the diagonal elements of the Fock matrix. The absorption energies have to be considered in a β-spin scheme. The unoccupied $\sigma_u^{(\beta)}$ level lies above the top of the valence band by ≈ 4 eV. It should be stressed that the optical absorption energy in the CNDO method is not equal to the difference of the corresponding one-electron energies. Our estimate of the quantity sought for, however, exceeds the experimental value (3.28 eV for the UV transition).

When an additional electron is trapped by the V_K centre, the α and β patterns coincide and here the occupied σ_u level, describing the ground state of an exciton, lies above the top of the valence band by 1.2 eV. The latter energy corresponds to the final state of the system when a radiative tunneling electron transfer occurs (cf. Section 4 in [6]).

From Fig. 2 it can be also concluded that the crystal field, produced by non-point ions, splits the π_g state by ≈ 0.24 eV.

In our view, a group of occupied levels lies much below the valence band due to an inaccurate description of the electron repulsion.[3]) This is so also because the one-centre Coulomb integrals, γ_{AA}, are calculated according to the standard calculation scheme [1] where the s AO's are employed for *both* cations and anions. The values of the Coulomb and exchange interaction of chlorines are greatly overestimated because both the γ_{AA}, γ_{AB} values differ considerably depending on whether they are calculated with s or p AO's.

An analysis of the electron density distribution shows that the hole is almost entirely shared by two displaced anions, i.e. the traditional X_2^- model of a molecular ion in a crystal is confirmed. However, the standard CNDO scheme neglects the essential change of the one-centre Coulomb and exchange interactions which have to arise from the positive charge of two anions in the V_K centre.

Our calculation also neglects the electronic polarization of a crystal by the positively charged V_K centre. This should lead to an increase of the defect levels. This increase which is ≈ 0.5 eV [4], in our opinion, cannot qualitatively change our pattern.

2.2 H centre

The MC simulating an H centre is shown in Fig. 1 b, the corresponding one-electron levels in Fig. 2. The α-spin pattern is similar to that for both the free Cl_2^- and V_K centre. However, for the β spin the σ_g level falls *between* the π_g levels, whereas the unoccupied σ_u level lies much higher than in the V_K centre. The crystal field splitting of π_g levels is also greater (0.76 eV) than in the V_K centre. A charge distribution analysis confirms the Cl_4^{3-} model of the H centre.

Our ordering of the *one-electron* β levels for the V_K, H centres does not contradict careful calculation of the Cl_2^- ion [7] (because in the latter the adiabatic terms are given) but partly contradicts Fig. 19.3 of Stoneham [4].

Dienes and Smoluchowski [8] presented an estimate for the location of the H centre level based on a variation of the well-known Born-Haber cycle, which is formally

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[3]) For an excited V_K centre there arise two effects: (i) π_g or σ_g hole state rises above the top of the valence band, (ii) further nuclear relaxation in X_2^- leads to its fall into the valence band thus producing a valence band hole.

close to our σ_u level occupied by a hole. However, a comparison of our results is rather complicated.

3. Electronic Structure of Perfect Surface

3.1 Point-ion model

Along with the above-considered electron and hole centres, which are produced by irradiation of a perfect crystal, the crystal surface is an example of a "natural" imperfection leading to the appearance of Tamm's bands of surface states in the gap of a perfect crystal. It is known that three-dimensional calculations of a surface state in terms of quantum mechanics are hard. To our knowledge, no experimental data in this field have been reported for alkali halides. Since our approach to defect structure calculations is based essentially on the Madelung potential approach, it is reasonable, first of all to discuss a simple electrostatic model for the surface bands developed in [9]. In the latter papers chemical bonding is assumed to be entirely ionic, leading to an approximate relation for the "bulk" forbidden gap, E_{bg}, and the gap between surface bands, E_{sg}, split off from the conduction and valence bands, as follows:

$$\left. \begin{array}{l} E_{bg} = 2V_b - I + A \, , \\ E_{sg} = 2V_s - I + A \, , \end{array} \right\} \tag{1}$$

where V_b and V_s are the Madelung potential energies for a bulk and at a crystal surface, I is the ionization potential of the cation, A the electron affinity for the anion. From (1) one can easily obtain

$$\frac{E_{st}}{E_{bg}} = \frac{1 - \gamma}{2(1 - \mu)} \, , \tag{2}$$

where $E_{st} = \frac{1}{2}(E_{bg} - E_{sg})$ is the maximum surface state splitting, $\gamma = V_s/V_b$, and $\mu = (1 - A)/2V_b$. We shall use these relations below.

3.2 Semiempirical calculations with point ions outside MC

Quite recently we have undertaken calculations of both a perfect NaF crystal and its surface employing the CNDO method for the MC embedded in the crystal field of point ions outside it [10]. The MC has been chosen in the 16-atom form, i.e. as simulating a perfect crystal in I, whose four atoms lie at a crystal surface. Unlike a perfect crystal, the four planes in the MC (hereafter referred to as s, 1, 2, 3; each containing four atoms) have *different* Madelung constants; namely, 1.6813, 1.7553, 1.7416, 1.7476. More careful calculations show that the expansion of the electrostatic potential near a surface lattice site in spherical harmonics of C_{4v} symmetry leads to a small (≈ 0.05 at. units) change of the diagonal element of the Fock matrix and we have neglected this effect. On the other hand, we have taken into account the possibility of different charges on atoms of different planes. Due to the latter effect, a crystal potential in an anion lattice site at the surface can be written as

$$a_0 V_s = 1.6085 Q_s + 0.07382 Q_1 - 0.007818 Q_2 + 0.007044 Q_3 \, , \tag{3}$$

where a_0 is the lattice constant, $Q_{s,1,2,3}$ are atomic charges of different planes, the first three coefficients are contributions of the corresponding planes to the crystal sum, whereas the last coefficient is a contribution of all planes below the second one, i.e. of a semi-infinite crystal. (It has been assumed in (3) that a possible difference of the atomic charges in the same plane plays a negligible role here.) Charges $Q_{s,1,2,3}$ were obtained in the self-consistent surface calculations.

The principle result of both models (Sections 3.1 and 3.2) is that the calculated surface bands are produced mainly by the surface atoms. Surface calculations [10] based

on the Mulliken-Ruedenberg method (different considerably from the CNDO) and realized in both the MC and large unit cell models, indicate the same nature of surface states, i.e. the effect of dangling bonds in MC model is negligible.

The E_{st}/E_{bg} estimate is 0.024 which is close to the 0.021 value obtained for the simple model in Section 3.1.

3.3 Effect of non-point ions

In this section the surface calculation of the NaCl crystal with parameters derived in I and the crystal field produced by non-point ions is presented. The calculated crystal potentials for four planes are given in Table 1 together with the point-ion values.

Table 1

Crystal potentials in the non-point-ion model (in at. units)

plane	present paper*)		point-ion model
	anion site	cation site	
s	0.198	−0.274	0.2871
1	0.195	−0.295	0.2998
2	0.190	−0.301	0.2974
3	0.186	−0.304	0.2984

*) Parameters: $\xi_{Na} = 1.24$, $\xi_{Cl} = 1.51$. The effective ionic charges in both models are ± 0.9.

We used two 16-atom MC's — the same as in Section 3.2 and that in which eight atoms are at the surface. Both calculations show a negligible (0.01 to 0.02) difference of atomic charges in different planes, as in [10]. We have also observed, as in [10], a splitting of surface bands. Both calculations indicate, however, that the main contribution to the MO, corresponding to surface hole levels, comes from the second-plane anions. Unlike the latter, the electronic surface states (split off from the conduction band) are created by surface cations. Such a nature of hole states results directly from the wrong behaviour of crystal field potentials in the anion sites of the different planes; unlike the point-ion model the potentials are *reduced* below the surface. This effect contradicts the results of both the models of Sections 3.1 and 3.2 based on a Madelung potential approach and indicates that our MC model employing a potential of non-point crystal ions (calculated via the standard estimate of an electron repulsion in the CNDO in the valence basis set) fails to reproduce correctly the behaviour of the field near a surface. An inclusion of core electron wave functions might essentially improve these results.

4. F Centre on the Surface and in the First Plane below It

In recent years there have been several papers dealing with surface F_s, F_s^+ centres in alkali halide and MgO crystals. These are theoretical and experimental studies of their optical and spin resonance properties as well as of chemical reactions with their participation (see [11] and references therein). Of particular interest are theoretical studies of these defects for the clarification of the lyoluminescence mechanism when a coloured alkali halide is dissolved [12]. The analysis of luminescent kinetics indicates

the necessity to consider chemical reactions which occur close to a surface and on the boundary of two phases. A possible mechanism of these reactions is the tunneling electron transfer from a surface F centre. To estimate the efficiency of these reactions one has to know the change of the one-electron defect energy when it approaches the surface.

In [11] the surface F_s centre has been calculated in the NaCl crystal in the approximation of a rigid point-ion lattice as well as by means of the model potential method. Physically reasonable results are obtained if only the second method with the ion-size corrections of the neighbouring ions is used.

We have calculated the electronic structure of the F centres on the (001) surface, F_s, of the NaCl crystal and in the first plane below it, F_s^1. Since the change of the crystal field potential on the surface, according to our estimate, exceeds the bulk value only by 0.01 at. units, as a first approximation we used the AF parameters, which were derived in I for the bulk F centre with the AF at an anion vacancy.

The results are given in Table 2. From this table one can see that the F_s level greatly rises as compared to the bulk value, whereas the F_s^1 level is only slightly reduced.

Table 2

Calculated properties of surface F centres (energies in eV)

property	on the surface	first plane below a surface
$E_b - E_{s(1)}$	2.75	0.45
$E_1 - E_s$	3.20	3.20
spin densities*)		
on AF	0.06	0.7**)
nearest cations	0.18	0.02
nearest anions	0.027	0.01

$E_{b(s)}$ is the one-electron energy of the bulk (surface) F centre, E_1 the same in the first plane below the surface.

*) In at. units.
**) These figures are close to the bulk values (cf. Table 3 in I).

The spin density of the F_s centre on the nearest ions exceeds the bulk value by an order of magnitude. This obviously is not a trivial result of the crystal field change but seems to be the effect of dangling bonds with ions absent above the surface.

5. Conclusion

It was shown in I that different approaches in calculating an interaction energy of the MC electrons with other electrons and cores *inside* and *outside* the MC lead to a considerable surface effect in the CNDO calculations. This shortcoming in the calculation scheme was partly improved by calculating the electron interaction with atoms outside the MC in the same way as with those inside it. On the other hand, this leads to unrealistic results for the band structure of the perfect crystal if the standard parametrization [1] or the parameters [13] are used. In our view, this indicates that the reasonable results obtained earlier are mainly due to the cancellation of two effects: (i) non-optimum choice of parameters and (ii) the point-ion model used in the crystal field calculations.

We derived new parameters which adequately reproduce the perfect crystal features and reflect the ionic nature of the NaCl crystal. However, the calculations for a series of the different kinds of defects (hole centres, 'pure' surface, and surface F centres) performed in this part of the paper indicate clearly that even the parameters, being specially calibrated to the perfect ionic crystal features, do not always permit to get satisfactory results for defect properties. This leads us to the following alternative: (i) either to specialize the parameters for the calculations of a certain type of defects (e.g. hole centres [14]) or, (ii) to derive a universal parametrization in which case the standard CNDO calculation scheme should be discarded. In our view such a parametrization, above all, requires a more accurate calculation of the electron repulsion energy (in particular, between the valence and the core electrons which involves discarding the valence basis set).

In conclusion it should be stressed that the accuracy of the location of defect levels within the gap of a perfect crystal essentially depends on (i) both the form and the size of the MC simulating the defect, (ii) the accuracy of the Madelung field calculation for a displaced ion, (iii) the reliability of the procedure devised to match the midpoints of the deep bands in two MC's (simulating the perfect and imperfect crystals, cf. Section 2.2 in [15]).

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