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Semiempirical Calculations of the Impurity Level Positions with Respect to the Perfect Crystal Bands

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The semiempirical calculation of the electronic structure of a perfect KCl crystal carried out within the framework of the large unit cell model is compared with those performed using the cluster model. The positions of the ground state one-electron levels of the impurity ions Tl^+ and Tl^{2+} within the gap are also calculated using molecular clusters of different sizes. The procedure which takes into account the crystal lattice polarization produced by a charged impurity is proposed for the calculation of Tl^{2+} levels. The electronic density distributions and the impurity level positions with respect to the KCl bands are compared for both the defects.

Полуэмпирическим методом Малликена-Рюденберга выполнены и сопоставлены расчеты электронной структуры совершенного кристалла KCl в модели расширенной элементарной ячейки и молекулярных кластеров разного размера. Выполнен расчет положения одноэлектронных уровней основного состояния примесных дефектов Tl^+ и Tl^{2+} в рамках молекулярных кластеров разного размера. Для расчета заряженного дефекта (напр. Tl^{2+}) предложен способ учета поляризации кристалла зарядом дефекта. Сопоставляется распределение электронной плотности вокруг обоих дефектов и положение индуцированных примесью локальных уровней.

1. Introduction

At present there exist many papers devoted to the calculations of impurity properties of crystals (e.g. [1 to 3]). However, attention is seldom paid to the position of the defect levels relative to the perfect crystal bands, the knowledge of which is necessary for estimates of the efficiency of such processes as optical and thermoionization of defects, chemiluminescence, adsorption, tunnelling recombination, and so on. The application of semiempirical quantum-chemical methods in the last decade has permitted to study the electronic structure both of defect and perfect crystals within the framework of the same computational scheme, which is necessary to determine with reliability the defect level positions within the perfect crystal gap.

Such calculations are carried out within the framework of two models: the molecular cluster (MC) [4] and the large unit cell (LUC) models [5]. The former deals with the electronic structure of a crystal fragment (perfect or containing an impurity) embedded into the electrostatic field of the rest crystal. The latter considers the electronic states of a crystal constructed of large unit cells, each of which may contain a defect, if an imperfect crystal is considered. Obviously in the LUC model defects are distributed periodically over the crystal. Proceeding within the MC model of the perfect crystal one is not able to connect the crystal fragment states obtained with the perfect band states in the Brillouin zone. Furthermore this model is of limited use for covalent crystals [6, 7] for which the LUC model appears to be most convenient.

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On the other hand, the study of an impurity electronic structure within the LUC model is embarrassed by the necessity to consider a rather large quasimolecule, for which the impurity bandwidth (caused by the interaction between the periodically distributed defects) has to be negligible. It is possible to simplify drastically the consideration of LUC for defects with high point symmetry [8]. However, the computational problems for the defects with low point symmetry (e.g. H and other molecular centres in alkali halides) are considerable. Moreover, the LUC model is in principle inapplicable for defects charged relative to the crystalline lattice (e.g. V_k , F^- , Tl^{2+} , Tl^0 , and other activation centres in alkali halides), that is why one should study such defects only within the MC model.

In order to estimate the positions of impurity levels within the crystal gap it is necessary to compare the results of calculations for *both* the perfect crystal and the crystal containing the impurity. The direct juxtaposition of two corresponding one-electron schemes is often unjustified for both models because of the discrepancies in the effective charges of atoms (and corresponding one-electron energies) surrounding the defect and similar atoms in a perfect crystal fragment which is caused by the rather small sizes of MC and LUC used. Moreover it is convenient to choose the shape of MC according to the point symmetry of the defect crystal (O_h for the point defects in the f.c.c. NaCl lattice sites). Such crystal fragments are usually charged [9] (see also below) due to which the corresponding one-electron levels are shifted. In turn when studying the *perfect* crystal it is reasonable to choose such a neutral MC which reproduces the stoichiometric of the perfect crystal (e.g. in form of the invariant Bravais parallelepiped which takes into account the translational symmetry of a crystal [9, 10]).

However, it should be noted that the comparison of a perfect crystal fragment with the cluster containing a defect and having the same size and shape, permits us to estimate the region around the defect over which its influence is spread.

In order to compare the results of two calculations (for perfect and imperfect crystals) we have suggested the procedure [10] which brings the middle-points of deep valence bands (e.g. 3s Cl bands in KCl) into coincidence, which implies an equal shift of all the occupied energy levels caused by the difference in effective charges of ions.

However, two problems still remain:

1. Is it more reasonable to compare the results of the defect structure calculation performed within the MC model with those of the perfect crystal obtained *either* within the LUC model (which is known to reproduce the perfect crystal properties more reliably) *or* to use the same MC model to study the perfect crystal?

2. How is it possible to take into account a polarization of the perfect crystal lattice by an excess defect charge when the charged defects are considered?

The purpose of the present paper is to clarify these questions using as examples the Tl^+ , Tl^{2+} centres in KCl crystals.

2. The Perfect KCl Crystal

The semiempirical method of Mulliken-Rüdenberg (selfconsistent charge and configuration) [10, 11] has been used for the calculations both within the MC and LUC models, the formulae and the parameters are given in [11]. The computational program applied makes use of a point symmetry of a quasimolecule (according to [8b]) which enables us to consider the fragment containing 125 atoms (9 spheres of ions around the central one, 311 basis functions) with moderate computational efforts.

In Table 1 the results for the perfect crystal KCl are given corresponding to the LUC containing 8 unit cells K_8Cl_8 , which reproduces the electronic states at the bottom

of the conduction band and at the edges of the s, p valence bands (Γ , X, and L points in the Brillouin zone [11]). The results for two MC's containing 27 and 125 atoms (3 and 9 spheres of ions around the central one, respectively) are also given there. The energy in the middle-point of the 3s and 3p valence bands, $-E_s^m$, $-E_p^m$, the 3p valence band width, E_p^w , the gap (ΔE_g), and the effective charges of ions ($|q|$) are assumed to be the most representative crystal properties. It can be seen from Table 1 that the valence bandwidths obtained for both MC's are underestimated as compared to those from the LUC model (due to a limited number of anions whose interactions are considered [7, 9]).²⁾

The effective charges of ions in the LUC are greater than those in the MC. Also a distinctive accumulation of electronic charge on the boundary atoms of the cluster is observed, which is accompanied with the splitting off of electron levels from the valence bands ("surface effect") caused by only partial compensation of dangling bonds by the electrostatic crystal field *outside* the cluster. The values of energetic properties in all these calculations appear to be very similar.

At a first sight one could expect that the enlarging of the MC should "stabilize" the results making them more close to those for LUC. However, it can be seen from Table 1 that this is not the case for most crystal properties except for the valence bandwidths. Perhaps this is a consequence of a few effects, namely 1. the change in the total charge of MC should cause a shift of one-electron levels; 2. different compensation of dangling bonds for different clusters by the electrostatic field of the rest crystal; 3. a contribution of surface-induced states in the evaluation of the energetic properties.

Taking all the above-said into account in order to estimate reliably the position of defect levels within the crystal gap, the results of the defect calculation performed within the MC model can be compared with those made in the framework of the LUC model for the perfect crystal.

Table 1

The features of the perfect KCl crystal obtained in MC and LUC models (energies in eV, charges in e)

model	$-E_s^m$	$-E_p^m$	E_p^w	ΔE_g	q
LUC [K_8Cl_8]:					
MR method	23.18	12.28	3.18	11.23	0.794
EH method [7]	22.83	11.83	2.93	13.21	0.94
MC [$K_{13}Cl_{14}$] ⁻ :					
MR method	22.60	11.65	1.90	10.96	0.762-0.807
EH method [7]	23.05	12.06	1.81	12.80	0.9-0.94
MR [$K_{63}Cl_{62}$] ⁺	23.50	12.56	2.64	10.51	0.731-0.794
exp. [15]		9.6	2.3	8.4	0.78
		(11.0)		(11.8)	

MR — Mulliken-Rüdenberg, EH — extended Hückel.

To compare the calculated values with experiment a valence band polarization correction (-1.4 eV) must be added to the experimental value of E_p^m , whereas the sum of polarization corrections for both bands (3.4 eV) must be added to the experimental ΔE_g [14, 15] (given in parenthesis).

In MC charge calculations the first value is given for the central ion.

²⁾ For a comparison also the results of the calculation of a 27-atomic cluster are given using the extended Hückel method (EH) [7]. It can be seen that some properties (especially q) differ considerably from those obtained by means of the Mulliken-Rüdenberg (MR) method.

3. Electronic States of KCl:Tl

We have considered the Tl impurity ion in two different charge states, Tl^+ , Tl^{2+} , which correspond to neutral and positively charged centres, respectively. These centres are studied experimentally in detail which facilitates theoretical investigations. The parameters for Tl are the same as in [7].

3.1 The Tl^+ centre

Due to the impurity perturbation two local states with symmetry a_{1g} split off above and below the 3p valence band, respectively. These are the mixed states whose molecular orbitals (MO's) contain 6s atomic orbitals (AO's) of Tl (with expansion coefficients of the order of 0.6 to 0.7) and 3p AO's of the six nearest anions. In Table 2 the values are given for both the absolute values of energies and for the a_{1g} level positions relative to the valence band edges in the KCl crystal for these levels. The perfect crystal is studied within the LUC model (Table 1) and to place defect levels within the gap the procedure [10] has been used³⁾. The calculations are carried out for two MC's containing 27 and 125 atoms being quite similar to those MC's used previously for the perfect crystal. For comparison also the results of the extended Hückel calculation of a 27 atomic cluster [7] are given.

Table 2

The position of impurity a_{1g} levels of Tl^+ , Tl^{2+} centres with respect to the edges of the valence band calculated for different MC's (energies in eV, charges in e)

MC simulating Tl^+	absolute energies of a_{1g} levels		positions of a_{1g} levels relative to the band edges ¹⁾		q_{Tl}
$[TiK_{12}Cl_{14}]^-$	-15.76	- 7.9	-2.31	2.37	1.15
$[TiK_{62}Cl_{62}]^+$	-16.36	- 8.26	-2.29	2.63	1.11
EH $[TiK_{12}Cl_{14}]^-$ [7]	-14.49	- 9.14	-1.52	2.02	1.28
Green functions [6]			-2.2	2.0	—
LUC $[TiK_7Cl_8]$	-15.55	- 6.32	-2.10	-3.95	1.12
MC simulating Tl^{2+}					
$[TiK_{12}Cl_{14}]^0$	-19.82	-11.91	-3.21	1.49	1.56
$[TiK_{62}Cl_{62}]^{2+}$	-20.34	-11.73	-4.35	1.10	1.53

¹⁾ For LUC $[K_8Cl_8]$ (Table 1).

It can be seen that the effective charges and one-electron energies of the impurity levels are similar for both MC's and agree quite well with the generally accepted mode of the Tl^+ centre ($q_{Tl} = 1$) and correspond to a small-radius centre. The EHT method shows a smaller split-off for impurity levels than the MR method. For comparison also the results of Green functions calculation [12] are given. Apparently the value of the split-off in the MR method exceeds also slightly the results of the latter [12]. It should be noted, however, that the results of [12] depend strongly on the perfect-crystal features employed. In [12] the latter have been taken from the APW calculation [13] which is known to underestimate significantly the p valence bandwidth. Bearing this in mind the correlation between our results should be denoted as quite

³⁾ When determining the energy in the middle-point of the 3s band for the MC containing the defect it is necessary to exclude the surface states as well as mixed states connected with the impurity whose influence can be the order of a few tenth of eV.

satisfactory. The energy difference between two a_{1g} levels in the 127 atomic cluster is only 0.3 eV greater than in the 27 atomic cluster.

According to the results of the Green function method [12] some induced halogen levels with different symmetry have to split off into the gap in addition to the two impurity levels. In our calculation these states connected with the anions of two nearest anion spheres appear to be quasilocal (situated within the 3p valence band). This discrepancy is possibly connected with the mentioned essential difference between the valence bandwidths in both calculations.

The obtained results which confirm the small radius of the impurity Tl^+ centre are also supported by an analysis of the electron density distribution around the defect. In Table 3 the effective charges are given for two clusters corresponding to the perfect crystal fragment and the similar one in which a central cation is replaced by thallium. In the defect crystal fragment the negative charge $0.26e$ is transferred from Tl to the six anions nearest to Tl^+ as compared with the anion charges in the perfect crystal fragment. The effective charge differences of the ions in the next nearest sphere around the central ion is less than $0.01e$ and becomes less than $10^{-4}e$ in the fifth sphere of ions. Thus the influence of the Tl^+ impurity is restricted to about *three* nearest spheres — in good agreement with a number of experimental and theoretical results (cf. [1]). Similar results are also obtained for the 27 atomic cluster.

Along with the two a_{1g} thalious levels there is one more mixed level having the symmetry e_g . It is situated within the 3p valence band and consists of both 6s AO from Tl (with expansion coefficient in MO ≈ 0.8) and 3p AO's from eight anions in the third sphere (III) (contrary to the *nearest* anions participating in the a_{1g} levels).

Table 3

Charge distribution for 125 atom MC's simulating the perfect KCl crystal and both Tl^+ , Tl^{2+} centres (charges in e)

coordinates of a sphere	number of ions	perfect crystal $[K_{63}Cl_{62}]^+$	Tl^+ $[TK_{62}Cl_{62}]^+$	Tl^{2+} $[TK_{62}Cl_{62}]^{2+}$
000	1	0.731	1.11	1.53
100	6	-0.731	-0.775	-0.705
110	12	0.730	0.721	0.717
111	8	-0.730	-0.731	-0.733
200	6	0.743	0.743	0.745
210	24	-0.741	-0.741	-0.739
211	24	0.743	0.743	0.744
122	24	-0.761	-0.761	-0.760

3.2 Tl^{2+} centre

In order to calculate the electronic structure of a charged (relative to the lattice) defect it is necessary to take into account the crystal lattice polarization due to its charge. We suggest that this can be achieved by adding to (subtracting from) the diagonal matrix elements of Fockian, $F_{\mu\mu}$, ($|\mu\rangle$ is an impurity AO) the lattice polarization energy due to a positively (negatively) charged centre. This procedure is completely similar to that applied in the theory of polarization corrections for interband transitions [14], which considers the decrease of the energy at the bottom of the conduction band and the increase of the energy at the top of valence band by the effect of excess electrons and holes caused by the interband transition (cf. [15] and comment to Table 1). When the electron is completely localized on the impurity the use of the estimations

[14, 15] is straightforward. Otherwise the additional self-consistence of these corrections must also take into account the excess electron (hole) density distribution around the defect (which is the case, e.g. for the quasimolecular V_k centre).

The results of such calculations are given in Tables 2, 3 for the Tl^{2+} impurity ion in two MC's containing 27 and 125 atoms. The *absolute* energy values are lowered drastically as compared to those for Tl^+ as a consequence of the change in the total charge of MC. This demonstrates the necessity of the procedure which brings the energy levels of different quasimolecules into coincidence [10]. The energy difference between the a_{1g} levels for the different clusters is greater in this case than for the Tl^+ centre and equals 0.7 eV. As compared to the Tl^+ the upper a_{1g} level containing the hole is situated closer to the valence band. (Obviously the neglect of the polarization correction should cause a significant lowering of the impurity level so that it could appear to be *within* the valence band).

In [16] the optical absorption bands of the positively charged mercury-like activator centres (Tl^{2+} , In^{2+} , and Ga^{2+}) in KCl have been qualitatively interpreted using a quasimolecule quite similar to the 27 atomic cluster used in our investigation. The authors of [16] have connected four absorption bands with the transitions from four levels with symmetry t_{1u} to the hole level. Two of these levels have been supposed to be quasilocal, whereas the two others have been estimated to be below the valence band. Our calculation shows that two such levels (consisting of 3p AO's from six nearest anions) appear to be quasilocal, one level is situated within the valence band near its bottom (possibly because of the overestimated valence bandwidth), and the fourth level is situated below the valence band, the latter two being constructed of the eight anions from the third sphere. The energy difference between the lowest level with t_{1u} symmetry and the hole a_{1g} level is equal to 4.6 eV which is slightly smaller than the experimental value [16]. The calculation shows also that there exist some quasilocal levels having *other* symmetry which might also contribute to the optical absorption (e.g. the e_u level which is constructed of 3p AO's from six nearest anions and is situated near the top of the valence band and the t_{2u} level which is constructed of AO's from anions in *both* first and third anionic spheres around the defect and is situated near the middle of the valence band).

The effective charges of the impurity obtained in both calculations are close and they show that nearly *half* the hole is distributed over the surrounding ions. (The significant covalency in the bonding between Tl^{2+} and the environment is supported by ESR data [17]). The electronic density distribution around the defect shows that — contrary to the Tl^+ centre — the electronic density has passed partly from the nearest anions to the impurity. The redistribution of the electronic density around the Tl^{2+} centre extends over a much broader range (five to six spheres) than in the case of the Tl^+ centre. It should be noted that the calculation of such an impurity centre in the framework of the Green functions method is a very complicated problem [18] though the procedure is also not free from semiempirical approximations.

An attempt of the calculation for the negatively charged (relative to the lattice) Tl° centre in the framework of the procedure described above results in the fall of the defect ground state into the conduction band. This is possibly caused by the significant difference between the actual value of the electrostatic field of rather diffuse 6p AO of Tl° and the employed value of the *point-ion* (Madelung) field ⁴⁾. Indeed an estimate using recent quantum-chemical calculations of the electrostatic field in crystal lattice sites, which take into account the *non-point-ion* effects [20], show that this effect may lower the position of the ground state level down to about 3 eV and lead to its position about an eV below the bottom of the conduction band in accor-

⁴⁾ Possibly this is the cause of a similar effect for an excited state of the F centre [19].

dance with experimental data. More detailed calculations for Tl° are now in progress.

Thus the calculation of defect electronic states within the MC model should be compared with the band structure calculations of the perfect crystals. The simple scheme proposed to take into account the lattice polarization due to the defect charge allows us to estimate the position of the ground state (hole) level of the Tl^{2+} centre and may be useful in calculations of non-point centres in crystals (e.g. for the molecular-like V_k centre).

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