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*Department of Quantum Chemistry, Leningrad State University***Molecular Cluster Approach to Magnesium and Calcium Oxide Crystals****II. F^+ and F Centres¹⁾**

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The model of the molecular cluster (MC) which has been applied for perfect MgO and CaO crystals is applied now to F^+ and F centres in these crystals. A method is proposed to estimate the optical transition energies within the SCCC technique. The calculated values of the absorption maxima of the F^+ and F centres are in reasonable agreement with experimental data. The procedure is also suggested to estimate the location of the defect levels within the forbidden gap of the perfect crystal. For comparison the analogous calculations of the ionic KCl crystal (perfect and with F centre) are given.

Das Modell des Molekülclusters (MC), das bereits für perfekte MgO- und CaO-Kristalle benutzt wurde, wird nun auf F^+ -Zentren und F-Zentren in diesen Kristallen ausgedehnt. Eine Methode wird vorgeschlagen, um die optischen Übergangsenergien innerhalb der SCCC-Technik zu berechnen. Die berechneten Werte der Absorptionsmaxima der F^+ - und F-Zentren befinden sich in vernünftiger Übereinstimmung mit experimentellen Werten. Es wird vorgeschlagen, mit dieser Methode auch die Störstellenniveaus innerhalb der verbotenen Zone des perfekten Kristalls zu berechnen. Zum Vergleich werden analoge Berechnungen des KCl-Ionenkristalls (perfekt und mit F-Zentren) angegeben.

1. Introduction

Part I of the present paper (hereafter referred to as I) has been devoted to the perfect oxide crystals. Now we turn to the intrinsic defects in these crystals.

At present there are known a few attempts to calculate the absorption energies for F^+ and F centres in MgO (e.g. [1 to 3], see also [4]). These calculations are based, as a rule, on the point ion lattice approximation and do not take into account the perfect crystal at all. Consequently, the question about the localization of the energy levels of defect within the energy gap of the perfect crystal remains open.

The calculation of the F^+ and F centres within the framework of the molecular cluster (MC) approach, applied in I to perfect crystals, is of special interest because the properties of such intrinsic defects are determined completely by the nature of the host lattice atoms as distinct from the properties of the impurity ion (especially a mercury-like one, whose properties change only little when placed into a lattice). In contrast to the traditional methods of the F^+ and F centre calculations, where use is made of the known symmetry of the ground and excited states of a defect and the trial function is centred on the

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vacancy, the present MC approach does not make any suppositions about the symmetry of the defect states.

2. The F⁺ and F Centre Calculations within MC Approach

When choosing the form and the size of the cluster, simulating the defect in crystalline environment, one should represent correctly the point symmetry of the object (the translational symmetry is obviously absent in this case). We calculated the F⁺ and F centres in MgO and CaO crystals, considering the [Me₁₄O₁₂]³⁺ and [Me₁₄O₁₂]²⁺ clusters, respectively (Me = Mg, Ca). Such clusters are cubes consisting of 26 atoms, the central oxygen atom being removed and 1 or 2 electrons being added.³⁾

2.1 The calculation of the optical transition energy

At present the extended Hückel theory (EHT) [6] is widely used to analyze the electronic structure of the crystal lattice defects. This method completely neglects the interelectronic repulsion and therefore there does not arise any problem of calculation of the optical transition energy. The latter equals to the difference of the corresponding one-electron energies obtained. However, the method employed in the present paper (Section 2 and 3 in I), which is based on the approximation of Mulliken and Ruedenberg and contains the self-consistent charge and configuration procedure, does indirectly take into account the interelectronic repulsion and therefore a more rigorous determination of the optical transition energy appears to be necessary. We have taken advantage of the virtual (vacant) orbital approximation [7] to calculate the transition energy. Within the framework of this approach [7] the spin many-electron wave function of the excited state corresponding to the definite total spin is a linear combination of the determinants in which the highest occupied MO is replaced by the vacant one. In [7] the following formulae are derived for singlet-singlet ($\Delta E^{(1)}$) and singlet-triplet ($\Delta E^{(3)}$) transition energies:

$$\Delta E^{(1)} = \varepsilon_v - \varepsilon_o - I_{v_o} - 2K_{v_o}, \quad (2a)$$

$$\Delta E^{(3)} = \varepsilon_v - \varepsilon_o - I_{v_o}. \quad (2b)$$

ε_v , ε_o are the one-electron energies of the virtual and occupied MO's, I_{v_o} , K_{v_o} being the Coulomb and exchange integrals, respectively, which are calculated using these MO's. In the case of the F⁺ centre the doublet-doublet transition (${}^2A_{1g}$ - ${}^2T_{1u}$) takes place. One can also generalize formula (2) for this case

$$\Delta E^{(2)} = \varepsilon_v - \varepsilon_o - I_{v_o} - K_{v_o}. \quad (2c)$$

In the case of the F centre singlet-singlet (${}^1A_{1g} \rightarrow {}^1T_{1u}$) and singlet-triplet (${}^1A_{1g} \rightarrow {}^3T_{1u}$) transitions occur, so formulae (2a) and (2b) should be used, respectively. In nonempirical calculation by the Hartree-Fock-Roothaan method one must calculate the quantities I_{v_o} and K_{v_o} exactly, reducing them to the two-electron integrals on the atomic functions. As for the approximate MO LCAO methods, it is expedient to calculate I_{v_o} and K_{v_o} within the *same* approximations which have been adopted in the calculation of the one-electron energies ε_v and ε_o . In [8] it has been shown that the Mulliken approximation, basing on

³⁾ The F⁺ centre calculations have been performed both without the lattice distortion around the oxygen vacancy as well as considering this distortion (using estimate [5]). However, the results obtained are almost the same.

which the formulae presented in I are derived, as well as the ZDO (zero differential overlap) approximation are in fact equivalent. The ZDO approximation corresponds to the use of an orthogonal atomic basis. Therefore, when changing the basis to the symmetrically orthogonalized (Löwdin's) one, the integrals I_{v_0} , K_{v_0} should be calculated basing on the ZDO approximation. These integrals were estimated by us using the atomic one-centre integrals γ_{AA} and the two-centre integrals γ_{AB} , the former being easily evaluated from the atomic spectroscopic data and the latter being calculated according to formulae of Ohno [9] and Mataga and Nishimoto [10] which are widely used in the molecular calculations.

2.2 The estimate of the position of F^+ and F centre levels within the gap

In spite of numerous calculations of the F centres in alkali halides and oxide crystals there exist at present only a few attempts to estimate the positions of defect levels in the energy scheme of the perfect crystal. In [11] the bottom of the conduction band as well as the local F centre levels in a KCl crystal have been calculated basing on the model potential method. In [2] it is estimated from the comparison of the F centre calculation in MgO crystals with the *experimental* estimate of the energy of the valence band top, that the ground state lies 3.5 eV below the top of the valence band. This result is apparently caused by the fact that, as it is well known, the employed point ion lattice approximation produces too deep defect levels (cf. [11]).

When calculating a cluster with a defect, one obtains a group of energy levels originating from the oxygen $2p$ states and which can be considered as the valence band states disturbed by the defect. In order to estimate the position of the defect levels within the energy gap of the *perfect* crystal, one should compare the calculated one-electron energy levels obtained for a cluster containing a defect with those for the cluster simulating the perfect crystal.

The perfect crystal is usually represented by a cluster of the same size and the same symmetry as the imperfect one [12, 13]. The comparison is then reduced to the direct transfer of the defect energy levels into the scheme obtained for the cluster simulating the perfect crystal. However, it has been shown (Section 2 in I) that the energy scheme of the perfect crystal is reproduced much better by a cluster having the form of a "large unit cell" (LUC). Therefore, in order to estimate the location of the defect levels it should be proposed to compare the energy levels obtained for the cluster simulating perfect crystal and having LUC form with those belonging to the cluster with defect. In the case of point defects in cubic crystals the corresponding clusters have *different* symmetry and size, but they represent correctly the symmetry of each of the objects (cf. [14]).

We have seen that the clusters simulating a crystal containing a defect have an electrical charge (as distinct from a cluster simulating the perfect crystal). Our calculations show that one-electron energies usually depend on the total charge of the cluster (e.g. see Table 1 in I). Therefore, the direct transfer of the defect levels into the energy scheme of the perfect crystal seems to be incorrect. In such a case one can propose the following method to estimate the position of the local levels of the defect. As the width and nature of the oxygen $2s$ valence band remains practically unchanged in the cluster containing the defect compared to that simulating the perfect crystal, the possible procedure is to match the middle points of the $2s$ bands in both clusters and thus to estimate the position of the defect ground state within the energy gap of the perfect crystal.

Table 1
Energy transitions for F⁺ and F centres in oxides calculated
by means of the MC method (energies in eV)

| centre | cluster | number of electrons in cluster | separation between ground state level (a_{1g}) and the bottom of the perfect crystal conduction band | calculated energy transition *) | experimental data [4] |
|----------------|--|--------------------------------|--|---------------------------------|-----------------------|
| F ⁺ | [Mg ₁₄ O ₁₂] ¹⁹⁺ | 97 | } 8.88 | 5.5 | 4.95 |
| | [Ca ₁₄ O ₁₂] ¹⁸⁺ | 97 | | 4.24 | 3.7 |
| F | [Mg ₁₄ O ₁₂] ¹⁸⁺ | 98 | } 8.88 | 5.4; 4.9 | 5.0 |
| | [Ca ₁₄ O ₁₂] ¹⁷⁺ | 98 | | 4.17; 3.65 | 3.1 |

*) ${}^2A_{1g} \rightarrow {}^2T_{1u}$ for the F⁺ centre and ${}^1A_{1g} \rightarrow {}^1,{}^3T_{1u}$ for the F centre. Experimental values for the F centre correspond to the ${}^1T_{1u}$ transition. The magnitude of γ_{AB} is calculated using Ohno's formula [9].

2.3 Results of the MC calculations

The transition energies for F⁺ and F centres (Table 1), obtained following the above-described method, are in satisfactory agreement with the experimental data. The agreement is better when Ohno's formula is used. It is important that the considerable energy decrease in the maximum of the absorption bands of F⁺ and F centres in the sequence MgO → CaO is reproduced. The experimentally found shift of the F absorption band toward the long-wavelength region relative to the F⁺ band in the same crystal is reproduced as well. This result is in accordance with other calculations (e.g. [3]).

The calculated one-electron energy levels appear to possess correctly the symmetry of the ground (a_{1g}) and excited (t_{1u}) states of the F⁺ and F centres. However, the contribution of 3s Mg AO's from the third coordination sphere to MO, describing the ground states of the considered centres, is too large (close to

Table 2
Comparison of energy level scheme for a cluster simulating the perfect KCl crystal
with that simulating the F centre (in eV)

| cluster | number of electrons | bottom and top of 2s-band | bottom and top of 2p-band | bottom of conduction band ^{a)} | ground state energy (a_{1g}) | transition energy ^{b)} |
|--|---------------------|---------------------------|---------------------------|---|----------------------------------|---------------------------------|
| [K ₉ Cl ₆] ⁰ | 64 | -23.5; -23.1 | -13.1; -11.6 | -1.252 | — | — |
| [K ₁₄ Cl ₁₂] ⁺ | 97 | -24.21; -23.82 | — | — | -4.06 ^{c)} | 2.19 |
| model potential method [11] | | — | — | 2.1 ^{d)} | -3.8 | 3.6 |

^{a)} and ^{b)} Only for experimental data: ^{a)} -0.6 [15, 16]; ^{b)} 2.3 [16] (excited state lies ≈ 0.16 below the conduction band).

^{c)} Match of middle points of 2s bands leads to estimate 8.25 above the top of the 2p-band of the perfect crystal.

^{d)} Without polarization corrections.

the contribution of the 3s AO's of six nearest Mg atoms). This is indicative of the incomplete localization of the electron cloud on the oxygen vacancy in the framework of the present MC model⁴) and very likely causes the overestimated energy value of the centre ground state.

The obtained results for the F⁺ and F centres in MgO and CaO given in Table 1 should be compared with results for perfect oxide crystals (Table 1 in I). For comparison an analogous calculation has been carried out for a perfect KCl crystal and one containing an F centre (Table 2). The ground states of F⁺ and F centres are located within the gap (about 9 eV above the top of the valence band) in accordance with experimental data. The energies of the excited states lie however somewhat *higher* than the bottom of the conduction band. Apparently, this may be caused by: (i) the mentioned incomplete localization of the electron cloud at the vacancy and the corresponding overestimate of the ground state energy, (ii) the inaccurate representation of the conduction band states in the framework of the MO LCAO method and (iii) the inexactness of the transition energy calculation as well. It should be also mentioned that the excited state of the F centre is situated just below the bottom of the conduction band (≈ 0.06 eV in MgO) which appreciably exceeds the accuracy of the MC method.

3. Conclusion

Let us enumerate the main points of the MC calculation of the F⁺ and F centres in oxides.

1. A method is proposed to estimate the optical transition energies in calculations of imperfect crystals using the Mulliken-Ruedenberg approximation with SCCO procedure. The virtual orbitals and ZDO approximations using a symmetrically orthogonalized (Loewdin's) basis are used.

2. The calculated optical transition energies for F⁺ and F centres are in reasonable agreement with experimental data, however, the wave function of the F centre turns out to be delocalized which is apparently a shortcoming of the MC method.

3. A procedure is also presented to determine the location of *charged* defect levels within the energy gap of the perfect crystal. This procedure is applied to the F⁺ and F centres in the considered oxides.

Results of the calculation for the ionic KCl crystal (both perfect and containing F centres) are presented for comparison.

It should be noted in conclusion that similar calculations provide the opportunity to determine the effective charge of the impurity ions in the crystals with regard of the influence of the surrounding lattice (which can be significant in covalent compounds). This problem will be discussed in the next paper.

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⁴) A similar result is obtained also for the F centre in KCl (see Table 2).

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