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Latvian State University, Riga¹⁾

Semiempirical Calculations of Defect Properties in LiF Crystal

II. Electron and Hole Centres and Their Recombination ²⁾

By

E. A. KOTOMIN and A. L. SHLUGER

The electronic structure of F, H, V_k centres in a LiF crystal is calculated using the INDO semi-empirical method. Use of both, the modified calculating scheme and earlier derived parameters permit to reproduce quite well optical absorption energies for hole centres and confirm their model of F_2^- molecular ion in a crystal. The locations of defect levels with respect to the band edges of a perfect LiF crystal are discussed. The calculations of pairs of nearest F-H, F- V_k centres predict energies of their radiative tunneling recombination of about 1 and 1.4 eV, respectively.

Полуэмпирическим методом ЧИДП рассчитана электронная структура F, H, V_k центров в кристалле LiF. Применение модифицированной расчетной схемы и новых параметров позволяют хорошо воспроизвести энергии оптических переходов в дырочных центрах и подтвердить модель F_2^- иона в кристалле. Обсуждается положение уровней дефектов относительно зон совершенного кристалла LiF. Расчет пар ближайших F-H, F- V_k центров предсказывает энергии излучательной туннельной рекомбинации ≈ 1 и 1,4 eV, соответственно.

1. Introduction

The theoretical study of imperfect ionic crystals stimulates a fuller understanding of numerous processes involving defects in these crystals, in particular tunneling recombination of pairs of spatially well-separated electron and hole centres in alkali halides [2 to 4]. It is well known now that the tunneling recombination of F- V_k defects is predominantly radiative, whereas the efficiency of such a radiative recombination and the emission energy for primary Frenkel pairs of radiative defects in alkali halides — F,H centers — are still in question (e.g. [5]).

For the radiative tunneling recombination the Condon approximation is valid, i.e. nuclei are fixed at the moment of the electron transfer (so-called "vertical transition"). Evidently, such a "vertical" radiative tunneling transition is possible if the total energy of a pair of electron and hole defects in the initial state (electron is localized on an electronic, e.g. F centre) *exceeds* that for the final state when the electron is on a hole centre (e.g. H, V_k). The difference of these total energies gives an estimate of the emission light quantum. On the other hand, the electronic structure of hole (H, V_k) centres in alkali halides and especially the location of their levels with respect to the perfect crystal bands are almost completely unstudied and are of independent interest. The reproduction of known experimental features of these defects (e.g. absorption energies) could be the criterion that the earlier developed method [1] is capable to obtain other defect properties, in particular, to estimate *in principle* the possibility of the radiative tunneling recombination and to estimate its energy.

The purpose of this part of the paper is the calculation of the electron density distribution for H, V_k hole centres in LiF crystal, the location of their levels in a perfect

¹⁾ Rainis Avenue 19, Riga 226050, USSR.

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band gap, the estimate of their geometry and optical absorption energies, and, at last, the calculation of the mutual perturbation energy of close F, H centres and energies of radiative tunneling recombination of close F-H, F-V_k centres.

2. Defect Property Calculations

As it was said above, calculations of the electronic structure of defects were performed using a MC model. Their level locations are estimated according to the procedure of Section 4 of [1].

2.1 F Centre

The F centre was simulated by a 26-atom MC containing three spheres of ions around a vacancy. An extended basis set involved an additional wave function (AF) centred on a vacancy.³⁾ Its parameters obtained according to [11] are: $\xi_F = 0.75 r_B^{-1}$, $E_{\text{neg}}^F = \xi^2/2 = 7.65 \text{ eV}$, $\beta_F = -2.5 \text{ eV}$.

The threshold value of optical ionization and spin densities on the nearest cations and anions are close to the experiment and are plotted in Table 1. An outward 1%

Table 1
Calculated properties of the F centre in a LiF crystal

property	a)	b)	exp.
$E^F - E_{\Gamma_{1c}}$ (eV)	5.76	5.61	5.4 [10]
spin density on the nearest ions (at. units)			
cations	0.046	0.049	0.0219 ^{c)}
anions	0.011	0.014	0.0252

a) Without a shift of the nearest cations. b) With 1% outward displacement. c) After [33].

displacement of the nearest cations, taken similarly to the estimate for KCl [8], has relatively small effect. (It could affect, however, the efficiency of defect tunneling recombination.)

An exclusion of the AF from the basis set results in a sharp increase of the ground state energy of the F centre accompanied by a considerable delocalization of its wave function, i.e. a large overestimate of the actual spin densities. On the other hand, a variational F centre calculation within the framework of a rigid point-ion lattice [9, 10] gives rather reduced ground state energy. Therefore, the obtained results confirm the earlier noted fact [11, 12] that a simultaneous extension of a basis set and the use of a non-point lattice model permit to obtain a ground state energy close to the experiment. In doing so, the orbital exponent, ξ_F , should be calculated *self-consistently* taking into account the non-point nature of ions surrounding a vacancy.

2.2 H, V_k Centres

The generally accepted models of the hole H and V_k centres in halide lattices are X₂⁻ molecules oriented along the <111> and <110> axes in a LiF crystal, which have been presented as being based on optical and ESR spectra [3, 9, 13]. However, such a model is *not* capable of analysing either the charge redistribution around the defects or the location of their levels with respect to the band edges of a perfect crystal.

The semiempirical calculation of H, V_k centres using a MC model which is free from these shortcomings [14] requires knowledge of the displacements of ions both within

³⁾ For the first time this idea was applied to a hydrated electron [6] and later to F centres [7, 11, 12].

the centres and in their vicinity. Both experimental data and theoretical calculations indicate, however, a large number of displaced ions around these centres [9] which affects, first of all, defect level locations with respect to the perfect crystal bands. At the same time, optical absorption energies are determined mainly by the internuclear distance, R_e , within the X_2^- . Theoretical estimates for chlorides [9] predict R_e to be for an H centre slightly smaller, whereas for a V_k centre greater than R_e in a free Cl_2^- molecule. Estimates known to us of R_e for H and V_k centres in LiF [15 to 17] based on an ab initio calculation of a free F_2^- [18] confirm such a conclusion, but do not permit to obtain *unique* values of ion displacement around at least H centres [9]. This is the more so because there are other ab initio calculations of the F_2^- (e.g. [19]) predicting R_e essentially *different* from the value $R_e = 3.6$ at. units given in [18] which could greatly affect displacement estimates.

Strictly speaking, the self-consistent approach to the electronic structure of defects should also include displacement calculations [12]. It is the more important for the potential energy curves and reaction path calculations. However, the low symmetry of the defects under investigation and consequently a great number of parameters makes this problem almost unreal. On the basis of the good agreement of our potential energy curves for free F_2^- with ab initio ones [18] only R_e was optimized. Displacements of other ions were taken according to [15, 16]. We obtained thus $R_e(H) = 3.5$ at. units, $R_e(V_k) = 3.8$ at. units. The INDO method used is a simplified version of the unrestricted Hartree-Fock-Roothaan (UHFR) method, according to which hole states are first unoccupied in a pattern for a β spin.⁴⁾ Both the α and β patterns exhibit local states consisting to $\approx 95\%$ of 2p AO's belonging to two anions of the F_2^- molecule. These states in the α -spin pattern are given in Fig. 1. Occupied σ_g, π_u, π_g states for both α, β patterns fall below the valence band (cf. [14]) whereas a *vacant* σ_u level for β spin lies above it. The sequence of one-electron energies for β spin unlike the α -spin pattern does *not* follow an inverse sequence of the potential energy curves (cf. [20]). The β patterns for H and V_k centres differ by the location of the σ_u level which is above π_u states for a V_k centre, but below them for an H centre.

To calculate optical absorption energies two procedures can be used.

(i) The difference of *total* energies obtained during self-consistent calculations of the ground and excited states (ΔE_{SCF}).

(ii) An approximation of "frozen orbitals", based on Koopmans' theorem, leads to an estimate

$$\Delta E_{ij} = \varepsilon_i(F_2^-) - \varepsilon_j(F_2^-), \quad (1)$$

where $\varepsilon_{i,j}$ are MO energies corresponding to the X_2^- molecule (with internuclear dis-

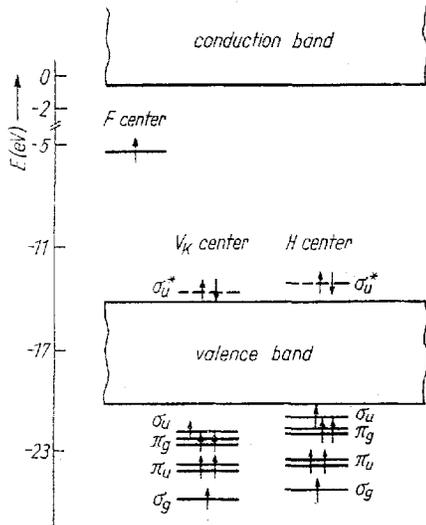


Fig. 1. The positions of one-electron levels of F, H, V_k centres with respect to the edges of the valence band of the perfect LiF crystal. The occupied states with α spin are shown only. σ_u^* indicates σ_u states of H and V_k centres which trapped an excess electron

⁴⁾ The analyses of hole density distributions argue for the F_2^- model for the ground states of both V_k and H centres. Unlike the X_4^{3-} model of an H centre in other alkali halides [3], our result for an H centre is directly due to its $\langle 111 \rangle$ orientation in LiF.

tance of X_2^- molecule).⁵⁾ This relation is *exact* for a free X_2^- molecule (for a given basis set) and has been used successfully earlier, e.g. for rare-gas molecules [25]. On intuitive grounds one could expect (1) to be valid also for hole centres provided MO's of the $H + e^-$, $V_k + e^-$ centres remain well localized.

Energies of their σ_u^* MO's are given in Fig. 1. The sequence of MO energies for $H + e^-$, $V_k + e^-$ is opposite to a sequence of potential energy curves of a molecular ion F_2^- and correlate with the well-known fact that the energy of the ${}^2\Sigma_u \rightarrow {}^2\Sigma_g$ transition by about a factor two exceeds that of the ${}^2\Sigma_u \rightarrow {}^2\Pi_g$ transition [3, 9].

The electron density distribution within the MC's simulating $H + e^-$, $V_k + e^-$ centres correlates also with defect level location with respect to the valence band edges. The occupied σ_u , π_g MO's consist mainly ($\cong 90\%$) of AO's belonging to the F_2^- molecule and are located *above* the valence band (see Fig. 1), and just below its top, respectively. Besides there exist *two* sets of π_u and σ_g states of $H + e^-$, $V_k + e^-$ centres having a nature different from the above given MO's. Their levels fall deeply *within* the valence band. The corresponding MO's contain only 30% of AO's from F_2^- along with a large contribution of the environment (which is different for the two sets). Hence these states can be considered as quasilocal ones.

The optical absorption energies of the H , V_k centres obtained in the two above-mentioned ways are given in Table 2. Both procedures give almost identical results for ${}^2\Sigma_u \rightarrow {}^2\Pi_g$ transitions. However, there is a serious discrepancy for ${}^2\Sigma_u \rightarrow {}^2\Sigma_g$ transitions caused by the above-mentioned quasilocal nature of the π_u , σ_g states of the $H + e^-$, $V_k + e^-$ centres which violates the validity of (1). Also the optical energies calculated by Δ_{SCF} are close to the experiment for *all* transitions.

It should be noted in conclusion that the σ_u MO's obtained for the $H + e^-$, $V_k + e^-$ centres are key properties for an estimate of a radiative tunneling recombination (TR) efficiency which is a well-known effect for electron (e.g. F) and hole (e.g. V_k , V_{kA} , etc.) centres in alkali halides (e.g. [2, 4]).

The estimate of the TR efficiency needs the knowledge of the emission quantum energy. It can be found as a difference of the total energies of a corresponding defect pair before and after electron transfer. Our experience shows that attempts to calculate the desired quantity employing the total energy difference of two pairs of MC's simulating separately *isolated* defects, before and after electron transfer, have led to unreasonable results. This is mainly due to the fact that the *total* MC energy depends on its size, charge, and shape much more than the eigenvalue spectrum (see (8) of [1]).

Table 2
Absorption energies calculated in two ways for H and V_k centres in LiF (in eV)

transition	H centre		V_k centre		exp. [9]
	a)	b)	a)	b)	
${}^2\Sigma_u \rightarrow {}^2\Pi_g$	1.74	1.83	1.4	1.4	1.65
${}^2\Sigma_u \rightarrow {}^2\Sigma_g$	4.03	3.2 6.94 ^{c)}	3.84	3.8 4.56 ^{c)}	3.48

^{a)} Δ_{SCF} procedure. ^{b)} Equation (1). ^{c)} For two sets of π_u , σ_g states. H , V_k centres were simulated by a 20-atom and 24-atom MC, respectively.

⁵⁾ Generally speaking there is also a *third* way to calculate an absorption energy using $\Delta E_{ij} = \varepsilon_i(F_2^-) - \varepsilon_j(F_2^-)$ plus the so-called Roothaan's corrections [21], cf. [22 to 24]. However, it is not applicable in the framework of our UHFR method.

Therefore, the most reliable way to estimate the TR energy is a simulation of defect pairs by a *single* MC (cf. [12]). We simulated pairs of nearest F-H, F-V_k centres by 27-atom clusters with a total charge +1. The ground states of these pairs correspond to electron localization on the hole centre (a vacancy is empty) but excited states are associated with its localization on the F centre. (Similar results have recently been reported for F-H pair in KCl [12].) The reliability of such calculations depends on which is greater: the electron affinity to the F centre or to the hole centre. As was shown in Section 2.1, the former property could be obtained correctly only employing an additional wave function centred on a vacancy.

The TR emission energy (Condon transitions) was calculated as a total energy difference for the MC simulating a defect pair in an excited and a ground state, i.e. by the Δ_{SCF} method. In doing so, we estimated $h\nu(\text{F-H}) \approx 1$ eV and $h\nu(\text{F-V}_k) \approx 1.4$ eV.

The experimental check-up of these estimates is of certain interest. Of special importance is a check-up of the prediction for F-H pair because of both the unsuccessful search of their radiative recombination in alkali halides (at $h\nu > 2$ eV) [5] and for understanding the mechanism of Frenkel defect creation and accumulation in ionic crystals (cf. [26, 27]).

The energy of the mutual perturbation of close defects can be obtained by the comparison of locations within a gap of MO energies of isolated and close defects. Thus we obtained for the nearest F-H pair the perturbation energy to be ≈ 0.5 eV (cf. [12]). Such estimates are vital to clarify the role of quantum-chemical interaction of primary Frenkel defects at their accumulation in crystals [12, 27].

3. Conclusions

The results obtained in this paper confirm that the modified calculation and parametrization schemes are able to reproduce correctly the electronic structure and geometry of the considered hole defects as well as some properties of molecules with different nature of chemical bonds. However, the procedure used for calculating the total energy, strictly speaking, does not seem to be quite consistent. Further search for a flexible way of describing the interaction of valence electrons with ionic cores, $V_{\mu\text{B}}$, is still necessary.

It should be noted that quite recently an idea [28] has been presented to introduce a self-consistency over a charge q in a one-centre feature $U_{\mu\mu}^A$ (cf. (7) of [1]) in the zero-differential overlap scheme similarly like it is done e.g. in the Mulliken-Ruedenberg method [29]. (These integrals are fixed in the standard CNDO/2 scheme [30].) The relation

$$U_{\mu\mu}^A(q_A) = -I_{\mu}^A(q_A) - (P_{AA} - 1) \gamma_{AA} \quad (2)$$

has been presented.

The dependence of an ionization potential, I_{μ}^A , on the μ -th AO population could be obtained from atomic spectra (similarly to the Mulliken-Ruedenberg method). Our scheme takes into account such a dependence indirectly through an optimization of E_{neg} , $P_{\mu\mu}^0$ parameters (equation (7) of [1]). In particular, the above-derived value $E_{\text{neg}}^{2\text{pF}^-}$ (Table 1 of [1]) is close to $I_{2\text{p}}^{\text{F}^-}$ for a charge $q = 0.75e$ obtained in the LUC calculation. On the other hand, the procedure (2) faces difficulties and becomes rather speculative if the dependence $I^A(q)$ is needed for the *virtual* states of cations (e.g. 2s Li⁺).

Of great interest is also a direct band gap calculation making use of the Δ_{SCF} procedure using the LUC (cf. [31]). However, our attempts and those of [32] in this way faced convergence difficulties. It seems to be due to an incorrect way of cal-

culating an intercore interaction in the total energy. Further investigations in this field are necessary.⁶⁾

The principle problem is the flexibility of parameters derived, i.e. whether the parameters for Li^+ can be used in calculations of defects with a quite different chemical bond and charge (e.g. of Li^0 centre in MgO crystal). The above given results for the F_2^0 , LiF molecules argue for it but the problem needs a more detailed study.

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⁶⁾ Our Δ_{SCF} calculation of the gap using the 27-atom MC yields narrowing of the initial gap, estimated as a difference of one-electron energies of about 9.5 eV.

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Quite recently the dependence of the tunneling recombination energy on interdefect separation has been investigated (Yu. TILIKS, A. SELUGER, Yu. DZELME, and E. KOTOMIN, Preprint, Internat Conf. Defects in Insulating Crystals, LAFI 30, Riga (USSR) May 1981 (to be published)). It has been shown there that polarization of a crystal due to defects must be taken into account.