

## FORMATION OF SELF-TRAPPED HOLES UNDER OPTICAL EXCITATION OF IMPURITY CENTRES IN LiF CRYSTALS

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**Abstract**—By the semi-empirical version of the HF method, referred to as INDO, combined with the embedded molecular cluster model, the electronic structures of  $O^{2-}-V_a$ ,  $Mg_c-O_a$  and  $Mg_c^+-V_aV_c$ -centres in LiF crystals were calculated. Their common feature is the existence of quasi-local states within the valence band, the optical transitions from which result in the formation of the self-trapped holes.

**Keywords:** LiF, INDO, O, Mg-containing impurity centres, electronic structure, photostimulated transformations, self-trapped holes.

The effect of optical delocalization of the holes from mercury-like  $A^{2+}$  centres ( $A = Tl, In, Ga$ ) in KCl crystal has been observed more than once [1–5]. Its dependence on the activator concentration has been studied and the following qualitative explanation has been suggested. The charged activator ion  $A^{2+}$  perturbs the occupied  $3p$  Cl states of at least two surrounding spheres of ions which results in either a split-off from the valence band edges or the formation of quasi-local states within the valence band [5]. The valence band holes arise due to the electron transition from these to the impurity energy level formed by the mixture of  $ns$   $A^{2+}$  and  $3p$  Cl states. Further, in the process, the holes created rapidly become self-trapped not far from the impurity. Evidently, this process of optical formation of self-trapped holes should take place for any point defect in insulating crystals where strong perturbation of the surrounding ion can produce local or quasi-local states of the uppermost valence band.

In order to ascertain whether this is true for LiF crystal, we have investigated theoretically both the electronic structure and the geometry of basic radiation and impurity centres in LiF–Li<sub>2</sub>O, LiF–MgF<sub>2</sub> and LiF–MgO crystals [6]. The centres under study contain impurity Mg and O ions with nearest anion and cation vacancies. We have succeeded in making more precise centre models, interpreting the optical absorption and luminescence spectra, and clarifying the mechanisms of several processes caused by these deep centres.

All the calculations were performed by the semi-empirical version of the HF method, referred to as

intermediate neglect of the differential overlap (INDO), combined with the embedded molecular cluster (MC) model [7, 8]. The interaction of ions entering the MC and outside it is treated in terms of the non-point polarizable lattice model [8]. The INDO parameters were calibrated specially for studying crystalline point defects [9]. Our basic method for the theoretical simulation of the centre geometry and the mechanisms of their photostimulated transformations is the calculation of the adiabatic surfaces of a crystal with deep centres with respect to the principal displacements from the regular lattice sites of the ions constituting the centres under study.

This means that at every point of the adiabatic surface we calculated the electronic structure of a crystal with a deep centre and its optical transition energies, thus being able, in particular, to study the sheet of the adiabatic surface of the excited states and thus to obtain the luminescence energies. Finally, we calculated the optical transition energies using the restricted configuration interaction technique, taking into account  $\approx 60$  single excited electronic configurations.

The distinctive feature of all the centres considered is the strong relaxation of the nearest ions surrounding the defect. Their calculated full-symmetry displacements are listed in Table 1; when calculating defects, 40–60 ions MCs were used. In particular, Fig. 1 demonstrates the MC used for the  $Mg_c^+-V_aV_c$  centre in LiF–MgF<sub>2</sub> crystal. The arrows indicate the displacement directions; their typical magnitudes are given in Table 1. The deep centres considered and the coordinates of the principal ions involved are listed in Table 2.

The impurity–vacancy dipoles  $O^{2-}-V_a$  are oxygen-

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Table 1. The fully symmetrical relaxation of the nearest ions for point defects in LiF (in units of the lattice constant  $a = 3.874$  a.e.). Sign  $\pm$  denotes outward or inward displacement, respectively

Defect	$V_a^+$	$V_c^-$	$O_a^{2-}$	$Mg_c^{2+}$	$Mg_c^+$
Ionic displacement	0.06	0.07	-0.13	-0.05	-0.08

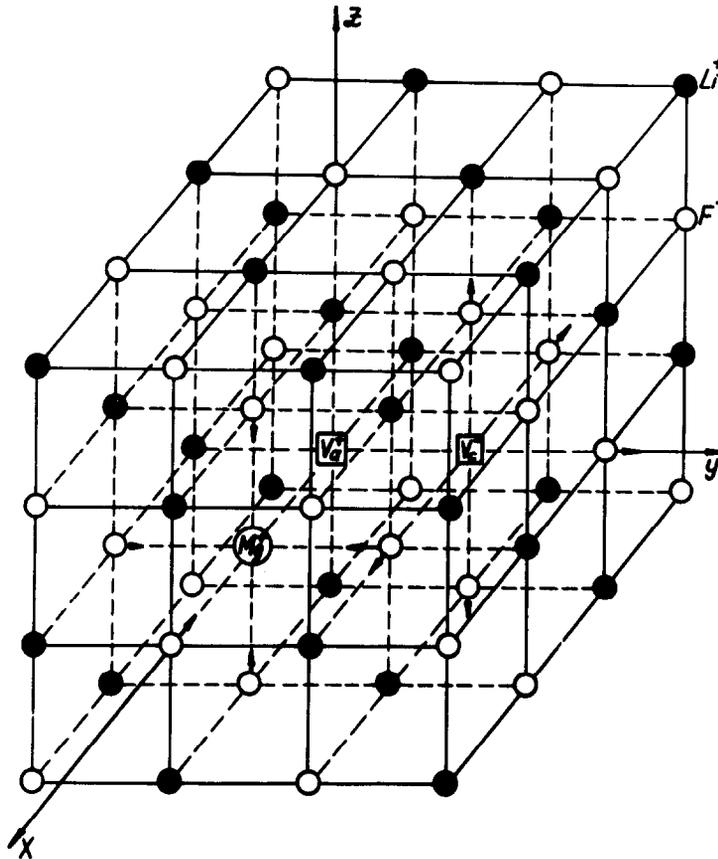


Fig. 1. A fragment of the crystalline lattice used for simulating the  $Mg^+ - V_a V_c$  centre.

Table 2. Distinctive features of radiation and impurity defects in LiF

Defect	Coordinates of its component	Energy of absorption and luminescence peaks maxima (eV)	
		Theory	Experiment
$O^{2-} - V_a^+$	$O^{2-} (0.05; 0.05; 0)$	7.07 (B)	
	$V_a^+ (1.0; 1.0; 0)$	7.4 (B) (3.4)†	6.5 (2.9)
		9.6–11.4 (C)	9.5
		7.5–9.0 (D)	
$Mg_c - O_a$	$Mg_c^{2+} (0.05; 0; 0)$	4.5 (B) (2.4)	(2.9)
	$O^{2-} (0.95; 0; 0)$	4.8 (B) (4.2)	5.5 (4.2)
		11–12 (C)	10.3
		6.8 (D)	6.4
$Mg_c^{2+} - V_c^-$	$Mg_c^{2+} (0; 0; 0)$		
	$V_c^- (1.0; 1.0; 0)$	2.5 (A)	The oscillator strength ( $\approx 10^{-5}$ )
$Mg_c^+ - V_c^- V_a^+$	$Mg_c^+ (0.06; 0; 0)$ $V_a^+ (1.0; 0; 0)$ $V_c^- (1.0; 1.0; 0)$	4.3 (A)	4.0

† Figures in parentheses indicate the maxima of the luminescence bands (A...D: see Fig. 2).

containing centres in LiF, experimentally the best studied ones [10]. The relevant absorption and luminescence peaks are listed in Table 2.

The  $Mg_c-O_a$  centres ( $Mg^{2+}$  and  $O^{2-}$  ions which are nearest neighbours) produce absorption in the 4.5–12 eV region and luminescence peaks at 2.9 and 4.2 eV, respectively [11] (see Table 2). The substituting  $Mg^{2+}$  ions in LiF– $MgF_2$  crystals have charge-compensator dipoles  $Mg^{2+}-V_c$ . The general view is that the ionizing radiation produces either  $Mg^+-V_c V_a$  [12] or Z-centres [13]. Their structures are not clarified; they are responsible for the absorption peak at 4 eV [12]. Our calculations have revealed that only the former centres could be radiation-induced; their electronic structure and geometry were also calculated (see Fig. 1).

The strong perturbation of the LiF crystal by these two kinds of defects leads to the appearance, in both the upper valence band and the conduction band, of quasi-local states whose wavefunctions are localized on the anions and cations of the two nearest spheres respectively [7]. The qualitative pattern of the one-electron energy spectrum typical for all the crystals considered is given in Fig. 2. Along with the quasi-local states, it reveals defect-induced occupied and empty local states. In particular, in the case of the  $O^{2-}-V_a$  centres, the occupied local states are due to the  $2p$   $O^{2-}$  atomic orbitals being split by the vacancy fields, whereas the empty state is localized near the vacancy [16]. The  $Mg_c-O_a$  centre is associated with (i) double-degenerate occupied states localized on  $2p$   $O^{2-}$  orbitals, (ii) another occupied state describing the MgO bond of the  $\sigma_g$  type and (iii) the empty quasi-local  $\sigma_u$  state. The wavefunction of the local states of both  $Mg^{2+}-V_c$  and  $Mg^+-V_c V_a$  centres are mainly due to the  $3s$  Mg orbitals. The possible optical transitions between the electronic states of this defect are plotted in Fig. 2, whereas absorption energies are given in Table 2. (Figures in parentheses show the

type of the corresponding transitions.) As is seen, the absorption spectra of all the defects considered contain the A- and D-type transition from the quasi-local states within the valence band. The peculiarity of the defects under study is that their A,D-excitations produce centres negatively charged with respect to the crystalline lattice ( $F-O^{2-}$ ,  $Mg_c^0 O_a^0$ ,  $Mg^0-V_a V_c$ ). This is why at temperatures below that of the  $V_k$  centre delocalization ( $\approx 140$  K in LiF) only spatially correlated pairs of  $V_k$  with the above-mentioned defects arise. The large excitation energies for  $O^{2-}-V_a$ ,  $Mg_c-O_a$  defects complicated the direct experimental optical observation of the  $V_k$  centres. They may be responsible in LiF– $Li_2O$  crystals for the recombination processes producing non-elementary luminescence kinetics at 2.9 eV excited in the region 5–10.5 eV [6]. Low oscillator strength of the optical transitions in the  $Mg^{2+}-V_c$  centre still prevents their experimental observation. The photobleaching of  $Mg_c^+ V_a V_c$  centres at 4 eV is associated with a new absorption band at 3.5 eV [12], which could be due to the  $V_k$  centres having absorption in LiF in the same region [12]. It is ESR which could help to clarify the nature of these centres.

Our theoretical calculations of the electronic structure of the complicated impurity centres in LiF have demonstrated that their common feature is the existence of quasi-local states within the valence band, the optical transitions from which result in the formation of the self-trapped holes ( $V_k$  centres) irrespective of whether we deal with cation or anion sublattice defects. The results obtained suggest that this effect should be observable for any centres which are charged or strongly perturb their crystalline ionic environment.

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## REFERENCES

1. Delbecq C. J., Ghosh A. K. and Yuster P. H., *Phys. Rev.* **151**, 599 (1966).
2. Kink R. A. and Lijdja G. G., *Fiz. Tverd. Tela* **9**, 1974 (1967).
3. Osminin V. S., *Fiz. Tverd. Tela* **14**, 2307 (1972).
4. Osminin V. S., *Fiz. Tverd. Tela* **16**, 560 (1974).
5. Osminin V. S., Zavt G. S., Zazubovich S. G. and Nijlisk A. I., *Izv. Akad. Nauk SSSR* **38**, 1235 (1974).
6. Mysovsky S. N., Nepomnyaschikh A. I. and Shluger A. L., *Opt. Spectrosc.* **63**, 129 (1987).
7. Shluger A. L., *Theor. Chim. Acta (Berl.)* **66**, 355 (1985).
8. Shluger A. L., Kotomin E. A. and Kantorovich L. N., *J. Phys. C*, **19**, 4183 (1986).
9. Shluger A. L. and Kotomin E. A., *Phys. Status Solidi (b)*, **136**, 673 (1981).
10. Radzhabov E., *Phys. Status Solidi (b)*, **136**, K149 (1986).
11. Nepomnyaschikh A. I. and Mironenko S. N., *Abstr. Sov. Conf. VU-82*, Moscow, p. 128 (1982).
12. Nepomnyaschikh A. I., Radzhabov E. A. and Egranov A. V., *Color Centres and Luminescence of LiF Crystals*. Nauka, Novosibirsk (1984).
13. Nink R. and Kos H. J., *Phys. Status Solidi (a)*, **35**, 121 (1976).

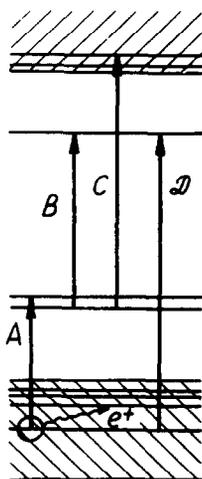


Fig. 2. Qualitative one-electron energy spectrum of LiF crystal with impurity centres and possible kinds of optical transition.