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On the role of magnesium in LiF:Mg,Ti thermoluminescent dosimeters

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Abstract. LiF doped with Mg and Ti is the most widely used thermoluminescent (TL) dosimeter for a large variety of applications. It has been argued that the Mg dopant is the most important defect in the TL process. Besides the common F-centre defects in LiF, optical absorption measurements have suggested the presence of Mg-related absorption bands at 380 nm (3.26 eV), and 310 nm (4.0 eV) when LiF:Mg is exposed to ionizing radiation, whose origin is not yet well understood. This work presents an investigation of the role of defects induced by Mg interstitials in LiF through electronic structure calculations. The calculations show that Mg interstitials induce a local lattice distortion characterized by the displacement of two opposite fluorine atoms, adjacent to the magnesium, away from their original sites by an average distance of 0.6 Å each, while the closest Li atoms are displaced by 0.1 Å. This defect introduces electronic states in the band-gap that can trap excess electrons produced during irradiation, thus enhancing the efficiency of the detector. Holes, on the other hand, are created and trapped in orbitals of mainly Mg-3s character. Additionally, the results suggest that irradiation can simultaneously remove a Li atom nearby a Mg interstitial; substitute a Li by a Mg atom or create a Li vacancy plus a Mg substitutional, giving rise to defects within the LiF gap that are more stable thermodynamically than the Mg interstitial itself. Interestingly, under irradiation the energy levels obtained for LiF:Mg-Li_{sub}+e⁻ (3.486 eV) and LiF:Mg+e⁻ (4.224 eV) defects are very close to the experimental absorption bands.

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1. Introduction

Lithium fluoride doped with magnesium and titanium (LiF:Mg,Ti) is the most commonly used thermoluminescent (TL) material. Its applications include occupational personal dosimetry, environmental monitoring, and medical and space dosimetry [1-4]. However, despite its success, the basic processes which give rise to this crystal's TL response to ionising radiation fields are not yet well understood [1-4]. Over the past 70 years, considerable work has been

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devoted to the identification of the defects responsible for this TL-response [5-16]. The difficulty of this challenge is demonstrated by the complex structure of the TL glow-curve, produced by measuring intensity of light emitted as the material is heated following irradiation. Fig. 1 shows an example of such a glow-curve, which can exhibit over 10 peaks [5-6]. Such peaks have been ascribed to specific defect states in the material, on the basis of phenomenological models that consider the flow of electrons and holes between trapped states [16]. Experimental studies have indicated that specific peaks can be assigned to traps created by Mg and Ti dopants [5-6].

Doped with Mg alone, LiF will produce TL peaks from room temperature to more than 300°C, where the absolute maximum is located around 220°C (see Fig. 1). The luminescence yields of LiF:Mg are relatively small [7]. The intensity, however, can be enhanced by a factor of 10 by co-doping with Ti, without distorting the curve [7]. From this, it can be inferred that Mg is responsible for creating the necessary traps, and that Ti serves to stabilize the traps. When LiF has been doped with other species, such as Cu and P, it has been shown that the Mg concentration remains the key parameter for achieving TL efficiency [8]. This study also showed that the Mg concentration affects the dose-response and linear energy transfer (LET: rate of energy deposited per unit length of a charged projectile [4]) dependence of the detector [8].

FIG.1 LiF:Mg,Ti TL glow-curve induced by 5 Gy of 100 keV average-energy x-rays displaying various peaks ascribed to different defect-states.

Having established that the role of magnesium dopants is to create trap states, we now consider what form these traps take. One possibility proposed to explain the peak at around 220°C is that it is due to clusters of Mg-Li_{vac} (Li vacancies) [6]. Early work suggested that holes would be trapped near complexes of Mg²⁺ ions and vacancies, while the TL centre would be a nearby colour centre (F-centre) defect [9]. Recent ab initio calculations [17] have confirmed that the F vacancy in LiF indeed gives rise to an F-centre that manifests itself in optical absorption spectra. Optical absorption studies of LiF:Mg exposed to ionizing-radiation have suggested the presence of Mg-related absorption bands at 380 nm (3.26 eV), and 310 nm (4.0 eV) in addition to the F-centres [9-15]. Several phenomenological defect models have been presented to explain the origin of these bands, particularly the one at 310 nm, but its true origin is still controversial. Mort [10], Crittenden et al. [11], and Seth et al. [12] concluded that the 4 eV band is associated to a Z₂-centre (a divalent magnesium ion adjacent to an F'-centre, that is an F-centre which has trapped an additional electron). On the contrary, a study performed by Klick et al. [9] found no evidence of a Z₂-centre in LiF:Mg, but this was attributed to the possibility that trapped hole bands obscure the Z₂-centre signal. Independently, Nepomnyashchikh and Radzhabov have been more categorical by affirming that there is no Z₂-centre formed in the LiF:Mg crystal, but instead there is a 3s→3p electronic transition in the Mg⁺ ions [15]. According to Mayhugh *et al.*, the 4 eV band is due to a trapped electron centre [13-14].

From the theoretical point of view, Shluger *et al.* [18] have investigated the electronic structure of O²⁻-V_a, Mg_c-O_a, and Mg_c⁺-V_aV_c centres in the LiF crystal using the semi-empirical intermediate neglect of differential overlap (INDO) method, a simplified version of Hartree-Fock theory. They concluded that only the Mg⁺-V_cV_a centres could be radiation-induced and the photobleaching of these centres at 4 eV is associated with a new absorption band at 3.5 eV, which could be due to the V_k centres having absorption in LiF in the same region [18]. Furthermore, they concluded that *“the common feature of the impurity centers in LiF is the existence of quasi-local states within the valence band, the optical transition from which result on the formation of the self-trapped holes (V_k centres) irrespective of whether dealing with cation or anion sublattice defect”* [18]. Density functional theory (DFT) calculations have been reported for the structure and stability of defects in a wide variety of materials [19-21]. A recent calculation [17] has focused on the F vacancy in LiF. However, to the best of our knowledge, there is no other published study about the role of the Mg defect in LiF that is based on DFT using hybrid functionals.

In this work we present first-principles electronic structure calculations of defect states induced by Mg-interstitials in LiF, and we analyse their role. We show that, electronically, such defects produce lattice distortion by the displacement of fluorine atoms, in the sense of introducing acceptor electronic states in the band-gap that can trap excess electrons during irradiation. We also analyse the geometric distortions associated with the introduction of defects.

2. Computational Details

Electronic structure calculations were carried out using the freely available, open-source code, CP2K [22-24] which implements density functional theory (DFT) using the Gaussian and plane waves (GPW) method [25]. A thorough test of basis sets in combination with several plane wave density cutoffs has been performed through the cell optimization of the pristine LiF using a 4x4x4 supercell (512 atoms). A difference of 0.04% (16.105 Å versus 16.112 Å) on the supercell's lattice constant at the PBE0 level was observed compared to the experiment for the DZVP-MOLOPT-SR-GTH basis set with a plane wave cutoff of 1000 Ry (see Table I of supplemental material). Similarly, for a 3x3x3 supercell (216 atoms), the resulting supercell's lattice constant was 12.076 Å, also in extremely good agreement with experiment, differing by only 0.07%. Core electrons were replaced by norm-conserving Goedecker-Teter-Hutter pseudopotentials [26-27], used in conjunction with the DZVP-MOLOPT-SR-GTH basis set [28] together with a plane wave cutoff of 1000 Ry for the finest of four grids in the multigrid solution of the Poisson equation for the density, which was adequate for the purposes of the present investigation. A convergence threshold of 10^{-6} Ha was used for the total energy self-consistency.

The PBE [29] exchange-correlation functional was used as a reference. PBE, as an example of a generalized-gradient approximation (GGA) functional, suffers from some well-documented limitations, such as underestimating the band-gap and misplacing defect levels. These are mostly due to the introduction of an important self-interaction error. As will be shown, in the present case of LiF, PBE is unsuitable for defect calculations. To overcome these limitations, we have assessed the performance of three different hybrid functionals that have been proved effective in correcting band-gaps and defect energy levels [30]. Firstly, we considered PBE0 [31-32], which features 25% Hartree-Fock (HF) exchange and the PBE semi-local functional, and the Minnesota M06-2X [33-34] functional that combines 54% HF exchange with a meta-GGA. Both are global hybrids, as opposed to range-separated versions that are generally more

suitable for extended systems. Besides, we also considered the range-separated screened hybrid functional, HSE06 [35-37]. We found this choice not to be particularly important in the present case because the defect-states are all well-localized already at the PBE level. Therefore, after carefully scrutinising the performance of these three functionals in comparison with available experimental data, a better agreement was observed with PBE0 data, so we decided to use PBE0 (see Table II of supplemental material). All calculations reported in the results section have thus been obtained with this functional. To reduce the cost of the Hartree-Fock calculation needed for the hybrid functionals, we used the auxiliary density matrix method [38-39]. Hybrids like PBE0 only correct for the non-locality of the exchange interaction. There is, however, a non-local contribution to correlation due to dynamical polarization, which results in the well-known van der Waals interaction. While bonding in LiF is mostly of ionic character, we nevertheless included van der Waals correlation corrections through Grimme's DFT-D3 pair potential [40]. Notice that the primary effect of this potential is on lattice parameters and internal geometry, which in this case includes structural distortions introduced by defects. Changes in electronic properties due to the Grimme correction are of second order. All calculations were spin-polarised using the unrestricted Kohn-Sham formalism.

3. Defect Calculations

Based on the result of the optimization test, a lattice constant of 4.028 Å was adopted for the cubic LiF unit cell [41]. The unit cell was replicated into a 3 x 3 x 3 supercell containing 216 atoms, and the cell volume and atomic positions were allowed to relax using the PBE0 functional. The relaxation convergence criteria were the following: a) 3×10^{-3} Bohr as the maximum displacement of an atom from the previous step; b) 1.5×10^{-3} Bohr as the root mean square (RMS) displacement of all atoms from the previous step; c) 4.5×10^{-4} Ha/Bohr as the maximum force on any atom; and d) 3×10^{-4} Ha/Bohr as the RMS forces on all atoms. By increasing the supercell size from 3x3x3 (216 atoms) to 4x4x4 (512 atoms) defect formation energies changed by less than 1%. Based on these results, we decided to use the supercell containing 216 atoms and to sample the Brillouin zone only at the Gamma-point. Five defect states were prepared, as summarized in Fig 2. Note that the illustrative structures shown in Figure 2 are the initial conditions before relaxation. To study the F vacancy defect, a lattice F atom was removed from the LiF bulk. We call this defect LiF-F_{vac} (Figure 2b). For the Mg dopant, four scenarios were studied: 1) insertion of a Mg atom into a tetrahedral interstitial position of LiF bulk [42-43], named LiF:Mg (Figure 2c); 2) substitution of a Li atom by a Mg

atom, called $\text{LiF:Mg-Li}_{\text{sub}}$ (Figure 2d); 3) insertion of a Mg atom into an interstitial position together with the creation of a Li vacancy (Li_{vac}) by removing a nearby lattice Li atom from the LiF bulk, named $\text{LiF:Mg-Li}_{\text{vac}}$ (Figure 2e); 4) substitution of a Li atom by a Mg together with the creation of a nearby Li_{vac} , called $\text{LiF:Mg-Li}_{\text{sub-Li}_{\text{vac}}}$ (Figure 2f). For each of these defective structures, the atomic positions were relaxed using the same relaxation convergence criteria indicated above. The final structures obtained after optimization will be discussed later. In addition, we considered these same systems with the addition of an unpaired electron that occupies the lowest-lying defect-state located within the large LiF gap of 14.2 eV [44]. In these cases, the negative charge was compensated with a positive uniform background. Any other induced defect-states in the gap observed at higher energies are empty. For comparison, we carried out calculations for pure LiF.

FIG. 2 Simplified illustrative structures for the initial configurations. Lithium, fluorine, and magnesium atoms are depicted as red, cyan, and black filled circles, respectively. Vacancies are indicated with an empty circle. The structures shown are (a) pristine LiF, (b) LiF with a fluorine vacancy, (c) LiF with a magnesium interstitial, (d) LiF with a substitutional Mg, (e) LiF with a Li vacancy plus a Mg interstitial and (f) LiF with a Li vacancy plus a substitutional Mg. The actual supercells used in the calculations contain between 215 and 217 atoms.

In addition, calculations for the F_2 molecule, and Mg and Li bulks have been performed to evaluate the formation energy of the defects. Lattice constants for the cubic Li and hexagonal

Mg unit cell were taken from the literature [45]. Similar to the LiF with defects, the unit cells were replicated into a 5 x 5 x 5 supercell containing 250 atoms and sampled at the Gamma-point to be consistent with the LiF calculations. The cell volume was allowed to relax using the PBE0 functional. The formation energies of the various charged defects were calculated as proposed in [46]:

$$E_f(X^q) = E_{tot}(X^q) - E_{tot}(bulk) - \sum_i n_i \mu_i + qE_F \quad (1)$$

where $E_{tot}(X^q)$ and $E_{tot}(bulk)$ are the total energies of the system containing the defect, X , and of the perfect crystal, respectively, using the same supercell; $\pm n_i$ are the number of atoms that have been added (+) or removed (-) from the supercell to form the defect of type i , and μ_i are the chemical potentials calculated in this work as the total energy per atom of the F_2 molecule, and Mg and Li bulk, using the same functional and basis sets as in the supercell calculations. E_F is the Fermi energy, and varies from zero, i.e. the valence band maximum (VBM), up to the conduction band minimum (CBM), i.e. the bandgap calculated for the system. For comparison between LiF bulk and the defected structures, the VBM of the supercell containing the defect was aligned with that of the bulk. In this work, the formation energy for the neutral systems has been computed for the same charge state $q=0$, while for the charged systems, a constant charge state $q=-1$ was considered and the formation energy was calculated at the same Fermi energy. Consequently, the comparison between two charged systems is expected to be independent of the Fermi energy.

The thermodynamic transition level (TTL), $\varepsilon^{therm}(q_1/q_2)$, of a defect is defined as the value of the Fermi energy, E_F , for which two charge states $q_1=0$ and $q_2=-1$ have the same formation energy, E_f , i.e. [46]:

$$E_f(X^0; E_F = \varepsilon^{therm}(0/-1)) = E_f(X^{-1}; E_F = \varepsilon^{therm}(0/-1)) \quad (2)$$

Using Eq. (1) and Eq. (2), the TTL can be obtained as described below:

$$\varepsilon^{therm}(0/-1) = E_{tot}(X^{-1}) - E_{tot}(X^0) \quad (3)$$

The problem with this approach is that the total energy (E_{tot}) calculated for charged periodic systems includes a contribution from the compensating background and is therefore not directly comparable with that of the neutral system. An alternative is to appeal to Janak's theorem [47], to write:

$$E_{tot}(X^{-1}) - E_{tot}(X^0) = \int_0^1 \mathcal{E}_{i+1}(N+n)dn, \quad (4)$$

where $\mathcal{E}_{i+1}(N)$ corresponds to the eigenvalue of the lowest unoccupied state ($i+1$) of the N -electron system with a neutral defect. A good approximation to the integral in Eq. (4) is to evaluate it via the trapezium rule using only the extreme points, instead of calculating $\mathcal{E}_{i+1}(N+n)$ for many values of n between 0 and 1 [48]. That is:

$$\varepsilon^{therm}(0/-1) = E_{tot}(X^{-1}) - E_{tot}(X^0) = [\mathcal{E}_{i+1}(N) + \mathcal{E}_{i+1}(N+1)]/2, \quad (5)$$

where $\mathcal{E}_{i+1}(N+1)$ is the eigenvalue of the highest occupied state of the $(N+1)$ -electron system, i.e. the charged defect system. These eigenvalues are all referred to the VBM and are accessible to our neutral and charged defect calculations. In addition, it is possible to estimate optical transition levels by considering the relaxation energy, E_{rel} , that corresponds to the energy difference between relaxed and initial charged defect structures [48], i.e.

$$\varepsilon^{opt}(0/-1) = \varepsilon^{therm}(0/-1) + E_{rel}, \quad (6)$$

According to Freysoldt et al. [46], the experimental meaning of the TTL is that for any Fermi-level position situated below $\varepsilon^{therm}(q_1/q_2)$, the defect is stable in charge q_1 , but if the Fermi energy is found above $\varepsilon^{therm}(q_1/q_2)$, then the charge state q_2 is stable. Optical transition levels, $\varepsilon^{opt}(q_1/q_2)$, can be observed in photoluminescence experiments [48], where the charged defect system is not allowed to relax.

4. Results

4.1 Defect energy levels

In the left panel of Figure 3 we show the total projected density of states (PDOS) for some of

the systems studied, namely: (a) pristine LiF, (c) F vacancy, (e) LiF:Mg, and (g) LiF:Mg-Li_{vac}. The systems with substitutional Mg exhibit PDOS similar to those with interstitial Mg. The energy levels are reported in Table I, below. The right panel shows the PDOS for the same systems with the addition of an electron. The zero was aligned to the valence band maximum (VBM), and the curves have been smoothed using Gaussians of 0.2 eV width. A side effect of this procedure is a slight broadening of the peaks. We have not portrayed the separate spin components for the sake of clarity.

FIG.3. Projected spin-up density of states as a function of energy for all the configurations studied, calculated at the PBE0 level. Configurations are labelled in the panels. Colours and line types indicate the contributions of the various atom types to the PDOS: F (blue), Li (orange), and Mg (green). The zero was aligned to the top of the valence band.

PBE results reported in Table I indicate a pristine LiF gap of 9.06 eV, a single defect-state for

LiF:Mg, which is essentially the Mg-3s state hybridized with orbitals of the neighbouring F and Li atoms, and two defect-states for the LiF:Mg-Li_{vac} as well as LiF:Mg-Li_{sub} while for LiF:Mg-Li_{sub}-Li_{vac}, any possible defect state is merged with the conduction band. The LiF:Mg state is occupied and located at about 2.27 eV, while LiF:Mg-Li_{vac} features an occupied (Mg dopant) and an unoccupied (Li_{vac}) state situated at around 2.56 eV and 1.46 eV below the conduction band minimum (CBM), respectively. For LiF:Mg-Li_{sub}, two states located at 1.09 eV (occupied) and 0.73 eV (unoccupied) below the CBM are observed. Upon the addition of an excess electron, the Mg-states shift very slightly upwards by 0.002 eV and 0.043 eV for LiF:Mg and LiF:Mg-Li_{vac}, respectively, but no other gap state appears within PBE. However, in the presence of an excess electron, LiF:Mg-Li_{sub} exhibits one defect state situated at 1.785 eV while LiF:Mg-Li_{sub}-Li_{vac}, shows two states localized at 1.095 eV and 0.73 eV below the CBM.

TABLE I. Kohn-Sham energy levels of the defects, $E_{\text{CBM}}-E_{\text{DS}}$, in eV.

Defect-state	PBE	PBE0	Experiment
LiF-gap	9.06	12.075	14.2 ± 2^{44}
F vacancy 1	3.420	5.064	5.061^{11}
F vacancy 2	1.629	1.866	---
LiF:Mg	2.270	4.534	4.428^{10-15}
(LiF:Mg+e ⁻) ¹	2.268	4.865	---
(LiF:Mg+e ⁻) ²	---	4.224	4.000^{10-15}
(LiF:Mg+e ⁻) ³	----	2.688	
(LiF:Mg-Li _{vac}) ¹	2.557	4.487	
(LiF:Mg-Li _{vac}) ²	1.461	1.584	
LiF:Mg-Li _{vac} +e ⁻	2.514	4.544	
(LiF:Mg-Li _{sub}) ¹	1.092	2.889	
(LiF:Mg-Li _{sub}) ²	0.728	0.919	
LiF:Mg-Li _{sub} +e ⁻	1.785	3.486	3.263^{10-15}
LiF:Mg-Li _{sub} -Li _{vac}	----	----	
(LiF:Mg-Li _{sub} -Li _{vac} +e ⁻) ¹	1.095	2.898	
(LiF:Mg-Li _{sub} -Li _{vac} +e ⁻) ²	0.730	0.922	

All hybrid functionals confirm the assignment of the above Mg defect-state, although at a deeper level. This is shown in Fig. 3(e) and 3(g) and numerical values are given in Table I for

PBE0. Similar results are observed for the Mg substitutional defects. While there are some discrepancies between the various hybrid functionals, they provide a similar general picture. Therefore, to avoid distracting attention from the main point of the present paper, we are only reporting the PBE0 results. Interestingly, all these defect-states are located at similar energies (PBE0 values around 4.5-5 eV), and very close to experimental data. For better comparison with the experimental data, Table I reports the energy difference between the conduction-band minimum (E_{CBM}) and the defect state within the LiF gap (E_{DS}); *i.e.* $E_{CBM} - E_{DS}$ as well as the thermodynamic transition level, $\epsilon^{therm}(0/-1)$, evaluated using equation (5). It has been suggested that comparing the Kohn-Sham energy levels directly with experimental results can be misleading [46]. The argument is that the optical transition, $\epsilon^{opt}(0/-1)$, (energy difference between the band gap and the energy of the photon emitted) is the energy level that would be observed in experiments like photoluminescence where, after the transition, the final charge state is not relaxed to its equilibrium configuration [20]. Note that in this case, the experimental band gap should be reproduced accurately by the DFT calculation [48], which is challenging for standard approximations such as LDA and GGA. Other studies have concluded that hybrid functionals that combine Hartree-Fock exchange with DFT exchange-correlation offer a feasible theoretical tool for determining the location of energy levels of deep defects within the band gap of bulk materials [49]. While this information is useful to identify these defect states and understand their nature, the most crucial aspect from the thermodynamic point of view is their stability. To this end, we computed defect formation energies as well as the thermodynamic transition levels, which will be discussed below. Afterwards, we evaluated the optical transition energy for the LiF:Mg+ e^- structure by computing the relaxation energy as the total energy difference between the charged systems before and after relaxation [50] and compared these values with experimental data in Table I.

4.2 Formation energy and thermodynamic transition levels

The formation energies evaluated with equation (1) at the same Fermi energy, $E_F = 0$ for all systems are reported in Table II while Figure 4 presents the results as a function of the Fermi energy relative to the VBM. At the PBE level we obtained an F vacancy formation energy of 9.28 eV, to be compared with the value of 8.2 eV reported in [17]. At the PBE0 level we obtained a slightly larger value of 10.33 eV. The PBE formation energies for the Mg, Mg-Li_{vac} and LiF:Mg-Li_{sub}-Li_{vac} defects are 8.15 eV, 7.8 eV and 2.64 eV respectively, *i.e.* slightly larger than the PBE0 values, except for LiF:Mg-Li_{sub} with 4.34 eV formation energy at the PBE level,

which is smaller than the PBE0 value.

Table II. Defect formation energies, E_f , and thermodynamic transition levels, $\varepsilon^{\text{therm}}$ (0/-), of various defect-states in LiF at the PBE0 theory level. Energies in eV.

Defect-state	$E_f(E_F = 0)$	$\varepsilon^{\text{therm}}(0/-1)$
LiF		
LiF-F vacancy	10.33	
LiF:Mg	7.463	
LiF:Mg+e-	15.34	8.32
LiF:Mg-Li _{vac}	7.29	
LiF:Mg-Li _{vac} +e ⁻	13.92	7.49
LiF-Mg-Li _{sub}	4.48	
LiF-Mg-Li _{sub} +e ⁻	11.58	8.00
LiF-Mg-Li _{sub} -Li _{vac}	2.53	
LiF-Mg-Li _{sub} -Li _{vac} +e ⁻	10.83	8.11

FIG.4. Formation energy as a function of the Fermi energy for the different defects within the LiF gap. The Fermi energy is aligned with the top of the valence band.

As observed in Table II and Figure 4, the results suggest that LiF:Mg-Li_{sub}-Li_{vac} is the most

stable of all defects, while the F vacancy is the least stable. For the charged system, the LiF:Mg-Li_{sub}-Li_{vac}+e⁻ defect also appears to be more stable than all the defects studied. The thermodynamic transition level (TTL), $\epsilon^{therm}(0/-1)$, calculated for LiF:Mg-Li_{vac}/LiF:Mg-Li_{vac}+e⁻ system is equal to 7.49 eV and indicated with a solid vertical red line in Figure 4. For the LiF:Mg/LiF:Mg+e⁻ system, the calculated TTL, $\epsilon^{therm}(0/-1)$, is equal to 8.32 eV and is indicated with a solid vertical blue line in Figure 4. For the LiF-Mg-Li_{sub}/LiF-Mg-Li_{sub}+e⁻ system, we obtained a TTL equal to 8 eV, which is shown by a solid vertical magenta line, while for LiF:Mg-Li_{sub}-Li_{vac}/LiF:Mg-Li_{sub}-Li_{vac}+e⁻ the value of the TTL is 8.11 eV and is shown by a solid vertical blue navy line in Figure 4.

5. Discussion

5.1 Defect energy levels

For the F vacancy – see Fig 3(c) – we observe an occupied state in the gap of *s* character located in the void created by the removal of the F atom (see Figures 5a and 5b). In pristine LiF, F-atoms are negatively charged at the expenses of the Li-atoms, due to their electronegativity. The removal of an F-atom frustrates this charge transfer, but the void sustains an electronic state that is still capable of accommodating this transferred charge. The LiF system with an F vacancy has an unpaired electron, and hence a net spin of ½. Figure 5a shows this electronic state as portrayed by the spin density isosurface of value 0.0065 e/Å³, while Figure 5b shows a contour plot of two-dimensional projection of the spin density in a plane that contains the F vacancy. These figures show that this state has unequivocally *s*-angular character and is centred at the F vacancy. Energetically, the defect is located at around 3.5 eV (PBE), 5.064 eV (PBE0) below the CBM. The PBE0 value of 5.064 eV is very close to the reported experimental value of 5.061 eV [11] (see Table I). Such agreement is of similar quality to values previously reported from *ab initio* many-body calculations, including quantum chemical correlated methods at the CASPT2(ROHF) level (5.22 eV) [17], many-body perturbation calculations including GW and Bethe-Salpeter for excitonic effects: GW₀@PBE + BSE (5.42 eV) [17], and BSE-corrected DFT approaches like TB-mBJ + BSE (4.9 eV) [17]. These were considered to provide unprecedented agreement with experimental results [17].

FIG.5a Spin density isosurface of the LiF:F vacancy. The grey and green symbols represent the F and Li atoms, respectively. The blue surface (value $0.0065 \text{ e}/\text{\AA}^3$) is an *s*-like spin density centred at the F vacancy site.

FIG.5b Two-dimensional contour plot of the F vacancy spin density. The central contour is the *s*-like density centred at the F vacancy, while there is a slightly negative spin density in the neighbouring atoms. Black circles indicate the location of the atoms in the plane of the contour.

Since Mg^{2+} is a divalent ion, the LiF:Mg system has no net spin. However, upon electron addition the $\text{LiF:Mg}+\text{e}^-$ defect has an unpaired electron that can be characterized by the spin density, similarly to the F vacancy. Contrary to PBE, hybrids exhibit two additional defect-states similar to the reported optical absorption results (Table I). The PDOS (Figure 3(f)) shows two occupied states and an empty state. From the thermoluminescence point of view, these occupied defect-states can be identified as trap-centres where holes in the valence band produced by ionizing radiation may be trapped. The energies of the defects relative to the CBM are reported in Table I as $(\text{LiF:Mg}+\text{e}^-)^1$, $(\text{LiF:Mg}+\text{e}^-)^2$ and $(\text{LiF:Mg}+\text{e}^-)^3$. The first state, $(\text{LiF:Mg}+\text{e}^-)^1$, can be identified with the Mg-3s state in the neutral system, LiF:Mg . The other two states, $(\text{LiF:Mg}+\text{e}^-)^2$ and $(\text{LiF:Mg}+\text{e}^-)^3$, are very interesting. As will be shown below, they are accompanied by a local distortion produced by the presence of the Mg-interstitial.

Furthermore, we notice that, for $\text{LiF:Mg}+\text{e}^-$, apart from the Mg-defect level, there is another occupied state with an energy that, at the PBE0 level, agrees quite well with the experimental value displayed in Table I (4.22 vs 4 eV), and an empty state at 2.688 eV, corresponding to $(\text{LiF:Mg}+\text{e}^-)^3$. Besides, we obtained a relaxation energy, $E_{rel} = 1.7$ eV for this system which, by considering the data in Table II, gives an optical transition level, $\varepsilon^{opt}(0/-1) = 8.32 \text{ eV} + 1.7 \text{ eV} = 10.2 \text{ eV}$. This implies that the energy of the observed photon emitted in the experimental absorption bands, E_{ph} , would be the difference between our energy band gap and $\varepsilon^{opt}(0/-1)$, i.e. $E_{ph} = 12.075 \text{ eV} - 10.02 \text{ eV} = 2.055 \text{ eV}$, which is smaller than the measured 4 eV absorption band by ~ 2 eV. Nevertheless, given the underestimation of the energy band gap by the PBE0, if we consider the experimental band gap [44] instead, then $E_{ph} = 14.2 \text{ eV} - 10.02 \text{ eV} = 4.18 \text{ eV}$. This value is in excellent agreement with the 4.22 eV value obtained from the Kohn-Sham eigenvalues for the $(\text{LiF:Mg}+\text{e}^-)^2$ defect (see Table I). This result suggests that, at the level of hybrid DFT, the relative difference in energy between the CBM and the KS energy level of the defect is a suitable approximation to the optical absorption band energy, as proposed previously by Alkauskas et al. [49].

In order to understand the origin of these states, we analysed the geometry together with the spin density. In LiF:Mg , the Mg sits in a tetrahedral interstitial position in the lattice and induces a small local distortion of the lattice through the displacement of two opposite nearest fluorine and one lithium atoms away from their original positions by distances of 0.6 Å and 0.1 Å, respectively. In the presence of radiation, i.e. when adding an excess electron, we observed

only small adjustments of distorted structure, with F-atoms moving further away from the Mg to 0.7 Å and the Li atoms moving back by roughly half the distance they moved in the neutral system (0.05 Å). The resulting spin densities of the LiF:Mg+e⁻ system are presented in Figures 6a (isosurface) and 6b-c (contour). Note in Figures 6b-c that atoms in the same plane of the Mg (black circles) are pushed away, while those in the planes below and above (white circles) are drawn in closer to the Mg interstitial. The excess electron, which is located in the space between the Mg and its closest Li, occupies mainly a Mg orbital of *p*-character (Figure 6a), which is quite understandable since the Mg 3*p* orbitals are the lowest-lying unoccupied orbitals.

FIG.6a Spin density isosurface of the LiF:Mg+e⁻. The grey, green and orange symbols represent the F, Li and Mg atoms, respectively. The blue surface (value 0.0065 e/Å³) represents the spin density.

FIG.6b-c Two-dimensional contour plots of the LiF:Mg+e⁻ spin density in planes containing the Mg-interstitial. Black circles indicate the location of the atoms in the plane of the contour, while white circles indicate atoms in the planes below and above. The largest contribution to the spin density is in the yellow region.

Regarding $\text{LiF:Mg-Li}_{\text{vac}}$ and $\text{LiF:Mg-Li}_{\text{vac}}+\text{e}^-$, no qualitative difference is observed between the hybrid functional and PBE, apart from a downward shift in energy levels. Both indicate an occupied and an empty state in $\text{LiF:Mg-Li}_{\text{vac}}$ and only one occupied state in $\text{LiF:Mg-Li}_{\text{vac}}+\text{e}^-$ as shown in Figure 3(h). Note in Figure 3(h) that in the presence of an excess electron, there is no defect level associated to the Li_{vac} and the only occupied state agrees very well with the Mg-defect level (4.534 eV for LiF:Mg versus 4.544 eV for $\text{LiF:Mg-Li}_{\text{vac}}+\text{e}^-$). This implies that in the presence of radiation the two defect states Mg and $\text{Mg-Li}_{\text{vac}}+\text{e}^-$ exhibit the same character and are very close in energy (0.01 eV). It is, therefore, very difficult to distinguish between these two defects purely on the basis of spectroscopic data. Only a systematic analysis of the formation energy and the TTL, as will be done below, can clarify this matter.

The spin-density isosurface and contour plot for $\text{LiF:Mg-Li}_{\text{vac}}$ are shown in Figures 7a and 7b, respectively. Notice that for the neutral system, i.e. without excess electron, the Mg displaces a Li atom from its site by ~ 0.76 Å and takes its place in the lattice in substitutional position (Figure 7a), while the actual Li vacancy is nearby in the cell but not directly involved. The unpaired electron locates in an *s*-like orbital in the interstitial region adjacent to the Mg defect (Figure 7b).

FIG.7a Spin density isosurface of the $\text{LiF:Mg-Li}_{\text{vac}}$. The grey, green and orange symbols represent the F, Li and Mg atoms, respectively. The blue surface (value $0.0065 \text{ e}/\text{\AA}^3$) represents the spin density.

FIG.7b Two-dimensional contour plot of the LiF:Mg-Li_{vac} spin density in a plane containing the distortional space created by the Mg-interstitial. Colours are assigned as in Figure 6b-c.

In the presence of radiation, i.e. for LiF:Mg-Li_{vac}+e⁻, the Li atom that was relocated by the Mg returns close to its original position (only 0.25 Å away) while the Mg returns to the interstitial tetrahedral position, creating a distortion similar to the LiF:Mg geometry. In this case, the displacement of the neighbouring Fluorine atoms is asymmetric; one moves by an averaged distance of 0.67 Å while the other by 1.122 Å. The Li vacancy does not appear to have a direct involvement into the process. Based on this geometry analysis, the possibility of generating clusters of Mg-Li_{vac} as proposed in a previous study [6] becomes questionable.

Similar to LiF:Mg-Li_{vac}, no qualitative discrepancy is observed between PBE and PBE0 for all the defects with the Mg substitutional. Also note that for these defects, and in contrast to interstitial Mg defects, we do not observe a lattice distortion. The neutral LiF:Mg-Li_{sub} exhibits two defects levels located at 2.889 eV and at 0.919 eV below the CBM. The 2.889 eV energy level could be associated to the unpaired electron of the Mg 3s state as observed through the spin density shown in Figure 8. In the presence of radiation, only one defect state situated at 3.486 eV is observed for LiF:Mg-Li_{sub}+e⁻. Due to the fact that Mg²⁺ is a divalent ion, there is no net spin. Interestingly, this defect energy level is located very close to the 380 nm (3.263

eV) absorption band observed in the experiment [9-15] with a difference of 0.223 eV, similar to the 0.224 eV discrepancy seen between the LiF:Mg+e⁻ defect and the 310 nm (4 eV) experimental absorption band (see Table I). A geometry analysis reveals that for the LiF:Mg-Li_{sub}, the Mg substitutional causes the displacement of six nearest F atoms away symmetrically from their original site by a distance of 0.155 Å and the closest Li atoms suffer negligible effect. While in the presence of an excess electron, the displacement of the six neighbouring F atoms is asymmetric where five of them move forward by 0.72 Å, 0.4 Å, 0.35 Å, 0.25 Å and 0.2 Å whereas the other one moves back by 0.06 Å.

FIG.8 Spin density isosurface of the LiF:Mg-Li_{sub}. The grey, green and orange symbols represent the F, Li and Mg atoms, respectively. The blue surface (value 0.005 e/Å³) represents the spin density

The energy levels obtained for the LiF:Mg-Li_{sub}-Li_{vac}+e⁻ defect are quite similar to those for the LiF:Mg-Li_{sub} by a difference in energy less than 0.01 eV, regardless of the functional. This suggests that they share the same character. The spin density indicates that the excess electron

is localised in the Mg-3s state and the geometry analysis reveals that the Mg substitutional induces the displacement of six nearest F atoms symmetrically in pairs, by 0.14 Å, 0.15 Å and 0.18 Å, while one F atom close to the Li_{vac} by 0.15 Å. At the same time, three neighbouring Li atoms move away from their original position; two by 0.11 Å and one by 0.14 Å.

5.2 Formation energy and thermodynamic transition levels (TTL)

From the data shown in Table II, we note that for a charge state $q=0$, i.e. for the neutral system, the LiF:Mg-Li_{sub}-Li_{vac} defect is the most stable of the five defects considered here, with a formation energy of 2.53 eV. This is lower by 1.95 eV, 4.76 eV, 4.93 eV and 7.80 eV than the LiF:Mg-Li_{sub} (4.48 eV) LiF-Mg-Li_{vac} (7.29 eV), Mg interstitial (7.46 eV) and the F vacancy (10.33 eV), respectively. For charge state $q=-1$ (i.e. for the charged systems), the difference in formation energy between LiF:Mg+e⁻ and LiF:Mg-Li_{vac}+e⁻ is 1.42 eV in favour of the latter. Consequently LiF:Mg-Li_{vac}+e⁻ has a higher probability to be created due to radiation exposure. Notice that this energy difference is actually independent of the value of E_F . Similarly, the LiF:Mg-Li_{sub}-Li_{vac}+e⁻ defect has a formation energy 3.1 eV lower than LiF:Mg-Li_{vac}+e⁻, which means it has a higher probability to be created during the irradiation process than any other defects.

From the experimental standpoint [46], the neutral LiF:Mg-Li_{vac} is stable when the energy level displayed in Figure 3(g) is located below the thermodynamic transition level (TTL) of 7.49 eV, while the charged LiF:Mg-Li_{vac}+e⁻ defect is stable when the energy level displayed in Figure 3(h) is situated above. The two defect energy levels shown in Table I for the neutral LiF:Mg-Li_{vac} are situated at 7.588 eV and 10.491 eV above the VBM, which are both above the TTL by 0.1 eV and 3 eV, respectively. This suggests that in the absence of radiation, the LiF:Mg-Li_{vac} defects are not stable and do not appear to be feasible. In contrast, as shown in Figure 3(h), the defect energy level observed for LiF:Mg-Li_{vac}+e⁻ is located 7.531 eV above the VBM, i.e. above the TTL by 0.04 eV. Consequently, such a defect is thermodynamically stable, which means that the Li vacancy is more likely to be created during the irradiation process, as excess electrons are required to stabilize it. Comparing with data shown in Table I, the defect energy level for LiF:Mg is situated 7.541 eV above the VBM and 0.779 eV below the TTL, which implies that such a defect is stable in its neutral configuration and hence feasible under normal, non-irradiation conditions. In the presence of excess electrons, i.e. for LiF:Mg+e⁻, the two defect

energy levels displayed in Table I are situated 7.851 eV and 9.387 eV above the VBM but 0.469 eV below and 1.067 eV above the TTL, respectively. Consequently, one can argue that the Mg defect (blue squares in Figure 4) with an excess electron correspond to an energetically suitable charged state. The relatively large formation energy for the Mg defect close to the valence band maximum (~ 15.3 eV) suggests that the Mg interstitial cannot trap excess electrons in its empty states. Instead, as it is shown in Figures 6 and 7, it creates a local distortion, thus inducing an electronic state that is lower in energy than the Mg empty orbitals. First-principles (PBE) molecular dynamics simulations show that the excess electron is stable in this interstitial space.

For the neutral $\text{LiF:Mg-Li}_{\text{sub}}$ we found two defect energy levels located at 9.47 eV and 11.44 eV above the VBM which are above the TTL by 1.47 eV and 3.44 eV. Consequently, these states are not stable for charge $q=0$. For the charged $\text{LiF:Mg-Li}_{\text{sub}}+\text{e}^-$, only one defect energy at 8.29 eV above the VBM is observed, which is situated above TTL by 0.77 eV. This means that $\text{LiF:Mg-Li}_{\text{sub}}+\text{e}^-$ is stable and energetically suitable. Concerning the neutral $\text{LiF:Mg-Li}_{\text{sub-Li}_{\text{vac}}}$, no defect levels are observed within the gap. Nevertheless, in the presence of radiation, i.e. of excess electrons, two defect energy levels at 9.20 eV and 11.18 eV appear above the VBM and are located above the TTL of 8.11 eV, by 1.09 eV and 3.07 eV, respectively. This implies that $\text{LiF:Mg-Li}_{\text{sub-Li}_{\text{vac}}}+\text{e}^-$ is stable and energetically suitable.

In summary, the formation energy and thermodynamic transition level analysis performed in this work suggest that the Mg defect in its neutral and charged states as well as the $\text{LiF:Mg-Li}_{\text{vac}}$, $\text{LiF:Mg-Li}_{\text{sub}}$ and $\text{LiF:Mg-Li}_{\text{sub-Li}_{\text{vac}}}$ defects in their charged state are acceptor levels, *i.e.* electron traps. Therefore, as stable defects, they will trap electrons generated by radiation. Irradiation can create Li and F vacancies while generating secondary electrons (and holes) by ionization. These secondary electrons can find a Mg trap and localise to form a charged Mg-e^- defect, which is stable as it is located above the TTL. At the same time, irradiation can simultaneously: a) remove a Li atom nearby a Mg interstitial, creating a $\text{Mg-Li}_{\text{vac}}$ defect; b) substitute a Li by a Mg atom inducing a $\text{LiF:Mg-Li}_{\text{sub}}$ defect; and c) create a Li vacancy plus a Mg substitutional to form a $\text{LiF:Mg-Li}_{\text{sub-Li}_{\text{vac}}}$ defect, which will also capture a secondary electron above the TTL. The $\text{LiF:Mg}+\text{e}^-$ and $\text{Mg-Li}_{\text{vac}}+\text{e}^-$ defects are very close in energy, both for interstitial and substitutional Mg.

We have also observed that the Li vacancy does not play a relevant role in the defect formation. Moreover, calculations of the $\text{Mg-Li}_{\text{vac}}$ defect in a larger supercell containing 512 atoms with

the Li vacancy located 6.5 Å away from the Mg (compared to 4.9 Å in the 216-atom supercell), show that the spin density is practically unchanged (see supplemental material). This suggests that the location of the Li vacancy is probably immaterial to the structural and energetic characteristics of the charged defect; i.e. Mg and Mg-Li_{vac} charged defects are essentially the same. The results of this study shed new light into the role of Mg dopants in LiF dosimeters. In the absence of other traps, e.g. Ti dopants, irradiation will remove electrons from the (occupied) Mg-3s orbitals leaving behind a hole, while the removed electrons will travel through the material until they find a suitable trap at a LiF:Mg, LiF:Mg-Li_{vac}, LiF:Mg-Li_{sub} or LiF:Mg-Li_{sub}-Li_{vac} defects. This interpretation is consistent with the suggestion of Mayhugh *et al.* [13-14] who argued that the “*TL-associated 310-nm (4.0 eV) absorption results from trapped electrons*” in contrast to others experiments [10-12, 15].

6. Conclusions

The most common traps in LiF are F vacancies created mostly by the removal of F-atoms due to irradiation [51]. The present results, however, suggest that interstitial Mg dopants can also trap electrons in locally distorted structures characterised by the displacement of neighbouring Li and F atoms. These charged defect states are thermodynamically stable. Consideration of these defects provides an interpretation for the observed 2.3-fold enhancement of the thermoluminescent response of LiF:Mg compared to pure LiF, when exposed to radiation [9], and for the increase in intensity of the 4 eV band as the Mg dopant concentration increases [12]. That is, in addition to the regular F vacancies [51], the Mg defects, which can be considered as intrinsic defects introduced during the crystal growth procedure as well as the LiF:Mg-Li_{vac}+e⁻, LiF:Mg-Li_{sub}+e⁻, and LiF:Mg-Li_{sub}-Li_{vac}+e⁻ charged defects created during the irradiation process, result all in additional traps for electrons and hence in a higher TL intensity.

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