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A study of the self-trapped exciton and F centre in MgF₂

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Abstract. The self-trapped excitons (STEs) and F centres in MgF₂ are studied within the extended-ion approximation. It is found that the STE is in fact a nearest-neighbour F–H pair with C₁ symmetry. The theoretical results for the spectra of the STEs and F centres are in good agreement with experiments. The stable F–H pairs converted from STEs are generated only at the hole excited state of the STEs according to the calculations of the adiabatical potential energy curve of the STE/FH pair. A model of the excited-hole hopping diffusion is proposed to explain the reorientation of the H centre and the formation of the F–H pair under cascade excitation.

1. Introduction

Frenkel pairs comprising a vacancy and an interstitial in the anion sublattice are generated by ionizing radiation in some insulators in which the electron–phonon coupling is strong. The mechanism of generation of Frenkel pairs in several solids, typically in alkali halides and alkaline-earth fluorides, has been studied extensively, and it has been generally accepted that they are generated as a result of the adiabatic instability of self-trapped excitons (STEs) [1–4]. Under conventional ionizing radiation, the STEs are the primary product of ionizing radiation in these crystals. They are produced as a result either of exciton relaxation or of trapping of an electron by a self-trapped hole which consists of an X₂⁻ molecular ion (X denotes a halogen atom). In any case, they are highly excited electronically and/or vibrationally when generated and de-excited to the STE luminescent states or to the Frenkel defects in the form of F–H pairs. In fact, only a proportion of the STEs are converted to F–H pairs. Usually, the de-excitation occurs through many intermediate excited states located below the conduction-band edge, and the de-excitation pathways are different from material to material. It has been reported that excitation of the STEs in the lowest triplet state, into both electron-excitation and hole-excitation bands, produces stable F–H pairs in most alkali halides [5–7]. These results indicate that there exist excited states of the STEs, which are transformed to defect pairs with high probabilities and yet cannot be reached by conventional excitation, but these excited states can be reached by the cascade process, initiated by photoexcitation of the STE at appropriate photoenergies. Thus cascade excitation can be used to enhance the yield of defect pairs in some materials in which their yield is extremely low under conventional band-to-band excitation. Also, it is of interest to investigate the defect formation in the excited states of the STEs.

MgF₂ is a wide-gap material having the rutile structure. The symmetry of the crystal structure is lower than that of the alkali halides and the fluorites; the width of the valence

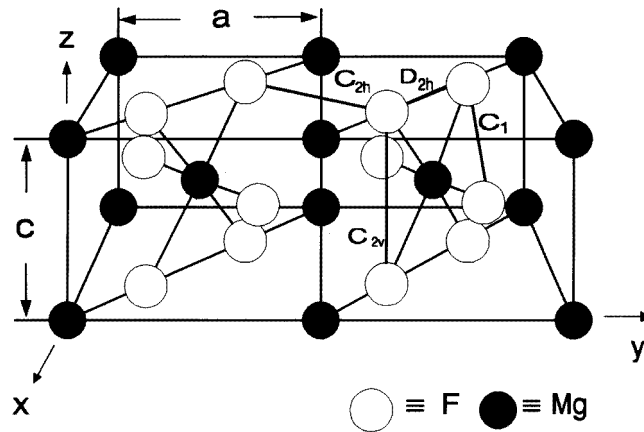


Figure 1. The lattice structure of MgF_2 . The F–F bonds for the four possible types of self-trapped hole are indicated.

band is much wider than that for the fluoride crystals with the cubic structure [8]. There are four inequivalent fluoride-ion pairs, labelled D_{2h} , C_{2h} , C_{2v} , and C_1 according to the site symmetry at the centre of the pair, as shown in figure 1. As a result, an STE can form in several different geometries. Which configuration is the most favourable for occupation by a STE is not yet very clear. Thus it is of interest to carry out theoretical studies of the STE and defect formation in MgF_2 . This material is important because of its use in optics, but also the absence of prior theoretical studies makes it timely to undertake such a study.

Formation of STEs and defect pairs in MgF_2 under conventional band-to-band excitation has been studied [9–12]. The transient optical absorption and luminescence following electron pulse irradiation have revealed the formation of a metastable state, which is responsible for the 3.22 eV emission and 4.51 eV absorption bands at 9 K [11]. The metastable state has been attributed to the spin-triplet STEs. The STEs in MgF_2 have a high formation efficiency. The energy required for creating an STE by electron pulse irradiation is only 28 ± 10 eV, and the yield of F centres near liquid helium temperature is lower than that of the STEs at least by a factor of 10^4 [11]. The energy needed to form a stable F centre by continuous irradiation at 5 K has been reported to be 4×10^5 eV [10]. These results imply that almost all of the electron–hole pairs created by band-to-band excitation are converted to STEs in the lowest state, and the branching to the defect pairs is extremely small. Recently, Tanimura and Itoh have found that photoexcitation of STEs in MgF_2 with a 308 nm laser pulse gives rise to efficient defect creation at 5 K. The yield of F centres increases greatly upon cascade excitation; the number of laser-induced F centres is proportional to the number of STEs annihilated [13]. According to their result that the quantum efficiency of conversion from STEs to F–H pairs is 0.1, the energy required to produce an F centre is only about 280 eV. Obviously, the STEs are converted to F–H pairs in the excited state of the STE with a quite high probability. It should be noted that the STEs in both alkali halides and alkaline-earth fluorides exhibit two distinct optical absorption bands: one due to the electron excitation and the other due to the hole excitation, but only a single broad absorption band has been observed in MgF_2 [13]. Williams *et al* suggested that the band is a composite, consisting of electron and hole transitions [11]. Thus, the most basic questions regarding the dynamic processes of F–H pair formation seem to be the following. (1) In which excited state of the STEs does the conversion from STEs to defect pairs take

place? (2) Do the STEs and F–H pairs for all separations lie on the same adiabatic potential surface representing this excited state of the STEs? (3) Is there any energy barrier against conversion from STEs to more distant F–H pairs by modest thermal activation? Thus, it is necessary to investigate defect formation under cascade excitation, based on theoretical calculations.

In this paper, we present a theoretical study of STEs and F centres and an investigation of defect pair formation using the extended-ion method. This paper is organized in the following manner. In section 2, the theoretical method employed is briefly described. In section 3, the equilibrium configuration of the STEs in MgF₂ is investigated, and the theoretical results for the spectra of STEs and F centres are given and compared with experiments. The adiabatic potential energy curves of the STE/FH pair are determined for the various states of the STEs. On the basis of the calculations, a model of the hole hopping diffusion is proposed in an effort to explain the F–H pair formation mechanism under cascade excitation. Finally, we summarize our conclusions in section 4.

2. The method of calculation

We developed earlier an approximate method by means of which it is possible to study a defect system involving one excited electron within the framework of the extended-ion approximation. In this approach, the defect electron, which is generally in an excited state (while all other electrons are in closed or nearly closed shells), is treated using the one-electron Hartree–Fock approximation. This means that all of the other electrons are treated as if they were frozen, as in the perfect crystal. In practice, one uses either the free-ion wavefunctions available in the literature (for cations) or uses those that are recalculated with an external Coulomb potential to simulate a point-ion lattice (for anions). The interaction between ions, as well as the polarizations, are treated classically using the $V(r) = Ae^{-r/\rho} - C/r^6$ type of pair potentials and the point polarizable dipole approximation respectively [14, 15]. The novelty of the method lay in the efficient and accurate way in which the various short-range terms in the one-electron Hartree–Fock equation were evaluated. A systematic use of the floating Gaussian (FGO) basis functions, in which 1s-like Gaussians with floating positions are exclusively used, was found to be both efficient and reasonably accurate. The advantage of the FGO basis is that it is possible to position the basis functions wherever the excited electron is likely to be present, which is very useful when the excited-electron wavefunction varies a great deal in the course of the lattice relaxation, as turns out to be the case for the STE in MgF₂. The other advantage is that it is possible to represent defect states of low symmetry in terms of a set of 1s-like FGOs positioned at suitably chosen sites. Details of this method are given in other publications [4, 16]. The self-trapped hole (STH) is a covalently bonded diatomic molecular ion F₂⁻. As the hole is transferred from one pair of fluoride ions to the next in the process of H-centre diffusion, it is necessary to represent this aspect in a quantum mechanical way, which cannot be done using the extended-ion approach. For this purpose, a CNDO code was interfaced with the above-described extended-ion method in such a way that the interaction between the excited electron and the diffusing H centre (in particular the charges of the H centre and the potential produced on the H-centre site by the excited electron) is properly evaluated at each step of the lattice relaxation. The CNDO parameters of the fluoride ions involved in the calculation have been adjusted from the standard values [21] so as to reproduce the bond length and the vibrational frequency of the molecular ion, as calculated by Tasker *et al* [22], as well as to reproduce the atomic electron affinity. This has been achieved in our earlier studies of the STE.

The evaluation of the matrix elements involving the Madelung potential of low symmetry in the MgF_2 lattice has been made on the basis of the Ewald method. A program package has been implemented which allows a self-consistent calculation of the defect electron wavefunction and the lattice displacements by means of minimization of the total energy of the system.

3. Results and discussions

3.1. The configurations of the STEs

It is believed that a self-trapped exciton in MgF_2 consists of an F_2^- molecular ion, or a hole localized on two fluorite ions, and an excited electron bound by the Coulomb field around the hole. The rutile structure is illustrated in figure 1, and there are four inequivalent fluoride-ion pairs, labelled D_{2h} , C_{2h} , C_{2v} , and C_1 according to the site symmetry at the centre of the pair. Thus there are four possible configurations of the STEs. For each possible configuration there could be two distinct types of STE according to the overall symmetry. When the excited electron is centred at the midpoint between two fluoride ions, the STE is modelled simply as being of the ' $\text{V}_K + e$ ' or the 'on-centre' type. When the excited electron splits from the hole centre (the F_2^- molecular ion) and localizes at an anion vacancy, the STE is in the 'off-centre' geometry. In practice, the calculations were performed in this way for the ' $\text{V}_K + e$ ' type of STE: the F_2^- molecular ion is placed in the V_K position along the axis which is described by the angles θ and ϕ for each site symmetry, and one set of optimized floating Gaussian basis functions is placed at the centre of the molecular ion. The position of the centre of the molecule, and the angles θ , ϕ are fixed during the calculation; the defect electron wavefunction, the hole charge distribution on the fluoride-ion pairs, and the lattice displacements are determined by minimization of the total energy of the systems. For the 'off-centre' type of STE, the adiabatic potential energy curves of the STEs are determined as functions of increasing F-H separation. With one set of optimized floating Gaussian basis functions placed on the nascent fluoride-ion vacancy, a designated fluoride ion is pushed by a discrete amount along the axis, and then all other ion positions, as well as the excited-electron wavefunction and hole wavefunction, are optimized. The equilibrium configurations are determined for the minimum energy in the adiabatic potential energy curves of the STEs for each site symmetry.

We present the results of our calculations of the equilibrium structure of the STEs in table 1. From table 1, it is easy to discern some interesting features of the STEs in MgF_2 , which are summarized below.

(1) The energies of the on-centre STEs are higher than those of the off-centre STEs for all four possible configurations C_1 , D_{2h} , C_{2h} , and C_{2v} . The energy differences are about 1.0–2.0 eV. This clearly indicates that the system relaxes spontaneously into an off-centre configuration. The way to understand the origin of the instability is to compare the energy of the excited electron in an off-centre STE (which we shall approximate as the energy of an F-centre electron) with that in an on-centre STE. The electron is much more strongly bound in an F centre (or equivalently in an off-centre STE) than in an on-centre STE. The gain in energy is typically between 1.5 and 4.0 eV. It is therefore understandable that after expending the lattice deformation energy, the STE relaxes into an off-centre configuration, and there is a total net gain of energy.

(2) The total energy of the STE having C_1 symmetry is lower than the total energies of the STEs with the other three configurations, for both the on-centre and the off-centre cases. The energy difference is about 0.9–1.7 eV for the off-centre STE. Thus, the C_1

Table 1. The possible configurations of the STEs in MgF₂. The total energy E_T and excited-electron energy E_e are given in eV. The bond lengths of the molecular ion, and the distance between the F centre and H centre are given in au. The position of the centre of F₂⁻, the orientation angles θ , ϕ , and the hole distribution of the V_K centre or H centre are also given in the table.

	C ₁	D _{2h}	C _{2h}	C _{2v}
On-centre				
E_T	8.38	10.71	9.08	9.17
E_e	-4.96	-2.34	-4.08	-3.99
R_{CM}	(6.61, -4.93, 4.34)	(4.40, -4.40, 0.00)	(8.81, -4.40, 5.82)	(2.73, -6.08, 2.91)
θ, ϕ	122.70, 283.50	90.0, 225.0	90.0, 148.5	180.0, —
q_1, q_2	-0.48, -0.52	-0.49, -0.51	-0.50, -0.50	-0.52, -0.48
Off-centre				
E_T	7.02	8.75	7.89	7.87
E_e	-6.43	-6.40	-5.92	-5.86
d_{F-H}	3.78	3.69	3.59	3.67
θ, ϕ	123.81, 276.19	91.3, 226.5	89.8, 148.0	173.87, —
q_1, q_2	-0.40, -0.60	-0.35, -0.65	-0.46, -0.54	-0.47, -0.53
$l_{\text{bond length}}$	3.42	3.63	3.60	3.63

configuration is the most favourable one as regards occupation by the STE. This result is in agreement with some earlier speculations [17, 6]. H centres in MgF₂ have been studied by means of EPR in crystals exposed to neutron irradiation at low temperature; as Ueda indicated, an H centre is an interstitial fluoride atom bonded to a lattice fluoride ion, with the hole symmetry corresponding to the charge states F^{-0.4}-F^{-0.6} [17]. This result is in good agreement with the hole charge states of the STE having the C₁ configuration, as shown in table 1. Therefore, the STE is in fact a nearest-neighbour F-H pair with the C₁ configuration in MgF₂ crystals; the distance between the F centre and the H centre is 3.88 au, and the bond length of the F₂⁻ molecular ion is 3.42 au in the equilibrium configuration. Only the STE with the C₁ configuration is discussed below.

3.2. Spectra of the F centres and the STEs

The spectra of the F centres have been widely studied in experiments. Blunt and Cohen first identified an absorption band near 260 nm for x-irradiated MgF₂ as being due to the F centres [18]. Facey and Sibley, working with electron- and γ -irradiated MgF₂, further substantiated this identification of the 260 nm band, and determined that the F centres are produced by a photochemical mechanism, rather strictly by momentum-transfer processes. A small luminescence band is observed at about 410 nm, excited by 254 nm light incident on an unirradiated sample [19].

The results of our calculations for spectra of the F centres in MgF₂ are presented in table 2. The coordinate axes for the representation of the excited states of the F electron are shown in figure 1. Obviously, the 2p_x and 2p_y states of the F electron are degenerate because of the symmetry in the X-Y plane. In practice, after minimization of the total energy of the system in the 1s F-electron state, the absorption energy is taken as the difference between the total energy of the system in the 1s F-electron state and in its corresponding (Franck-Condon) 2p excited state. The emission energy is calculated in a similar way, but, in this case, the total energy of the systems in the 2p excited states of the F electron has to be minimized. It is clear that the 2p_z state is responsible for the

Table 2. The absorption band and emission band of the F centre in MgF₂; the states of the defect electron are represented as 1s, 2p_z, and 2p_{x,y}, all of the energies are given in eV, and E_{pc} and E_{pe} are the peak energies in the calculations and in experiments respectively.

	E_e	E_t	E_{pc}	E_{pe}
Absorption band				
1s	-5.84	3.69		
2p _z	-0.74	8.50	4.81	4.85 ^a
2p _{x,y}	0.18	9.33		
Emission band				
1s	-4.56	4.52		
2p _z	-1.29	7.62	3.10	3.03 ^b
2p _{x,y}	-0.52	8.13		

^aTaken from reference [18].

^bTaken from reference [19].

Table 3. The absorption band and emission band of the STE in MgF₂; the electron and hole excited states of the STE are represented as 2p_e and 2p_h, all of the energies are given in eV, and E_{pc} and E_{pe} are the peak energies in the calculations and in experiments respectively.

	E_t	E_{pc}	E_{pe} ^a
Absorption band			
2p _e	11.68	4.66	
2p _h	11.61	4.59	4.51
1s	7.02		
Emission band			
1s ex⟩	7.02		
gr⟩	3.22	3.80	3.22

^aTaken from reference [11].

4.85 eV absorption band. Similarly, the emission band is due to the F electron returning from the 2p_z state to the 1s state. The results of our calculations are in good agreement with experiments.

The STEs in alkali halides and alkaline-earth fluorides exhibit two distinct optical absorption bands: one due to the electron transition, and the other due to the hole transition; however, only a single broad absorption band of the STE was observed for MgF₂ [11]. Williams *et al* suggested that the band is a composite, consisting of the electron and hole transitions in this case. We have calculated the absorption energies due to both of the excitations mentioned above. In practice, the equilibrium configuration of the STE in its low-lying state is taken from the off-centre configuration having C₁ symmetry, as shown in table 1. The axis of the electron 2p state is parallel to the molecular axis for the electron excited state of the STE. The hole excitation of the STE results from photoabsorption in the ${}^2\Sigma_{\mu}^{+} \rightarrow {}^2\Sigma_{\text{g}}^{+}$ ultraviolet transition, promoting an electron from the σ_{g} bonding orbital to the σ_{μ} antibonding orbital of the F₂⁻ pair, while the F electron is still in its 1s state. The results of our calculations are shown in table 3. The calculated electron- and hole-excitation energies of the STEs are very close, and both are in good agreement with the observed values.

Similarly, when the recombination processes of the electron-hole pairs occur, the system in the 1s state of the STEs will return to its Franck-Condon ground state. The emission

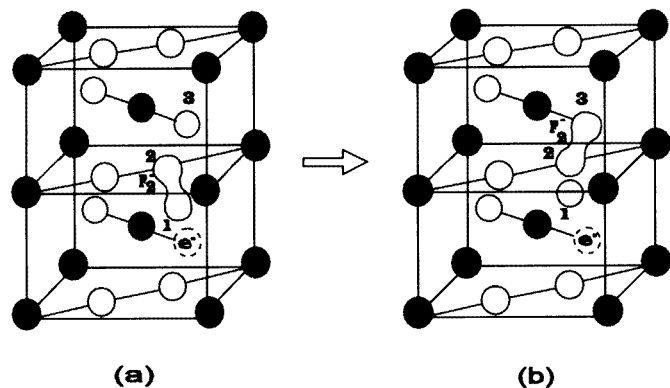


Figure 2. An illustration of the conversion of an STE to an F-H pair. (a) The original configuration, with fluoride ions 1 and 2 combined as the molecular ion F_2^- ; (b) the $(F-H)_{nn}$ configuration. When fluoride ion 2 becomes close to ion 3, bond switching may occur, and ions 2 and 3 are then combined as the molecular ion F_2^- .

energy of the STE is calculated as shown also in table 3. The result is in fair agreement with experiments.

3.3. The F-H pair formation mechanism

The defect formation mechanism is a subject of long-standing interest. The role of the STE in F-centre formation was recognized quite early [20]. The precise mechanism of the transformation of the STE state to an F-H pair has been the main subject of investigation. According to reference [13], the yield of the F-centre production in MgF_2 greatly increases when a cascade excitation occurs. The STE spectrum found for MgF_2 at low temperature transforms at about 190 K into the spectrum of F centres, representing F-H pairs of larger separation than in the STE (the nearest-neighbour F-H pair). For MgF_2 , the decay time of the separated F-H pairs is much longer than the STE lifetime at 190 K. The absorption spectrum changes subtly as the STEs convert thermally to more widely separated F-H pairs [11]. The following points are clear.

(1) The decay of the STE is simply the radiative or non-radiative recombination of the electron with the hole in the primitive F-H (nearest-neighbour) pair. In order to form an F centre and an H centre that survive beyond the STE radiative decay time, some of the nascent F-H pairs comprising the STE must achieve larger mutual separation; the energy required to convert an STE to a stable F-H pair is comparable to the energy of H-centre diffusion. The diffusion could be represented by covalent bond switching of the molecular ion F_2^- between two successive H-centre sites.

(2) Obviously, the transformation of the STE to an F-H pair occurs for an excited state of the STE. Is it the electron excited state or the hole excited state of the STE? Although stable F-H pairs are generated only by hole excitation of the STE in alkaline-earth fluorides, as Tanimura and Itoh pointed out [13], because only a single absorption band was observed for MgF_2 , the state which is responsible for the conversion of the STE into an F-H pair in the present case is not established yet.

In order to answer these questions, first we performed a search to establish a model of H-centre diffusion which requires the lowest activation energy. A possible model is shown

in figure 2. At first, the STE comprises an F centre and an F_2^- molecular ion with the covalent bond between the ions 1 and 2. When ion 2 approaches ion 3 either dynamically or thermally, bond switching may occur, leading to a new F_2^- molecular ion composed from ions 2 and 3, the next-neighbour H centre. This step corresponds to a reorientation of the H centre. The H-centre hopping motion in MgF_2 would involve a succession of a few basic steps, as described above. In order to perform this calculation, a set of three fluoride ions have been included in the CNDO part of the program.

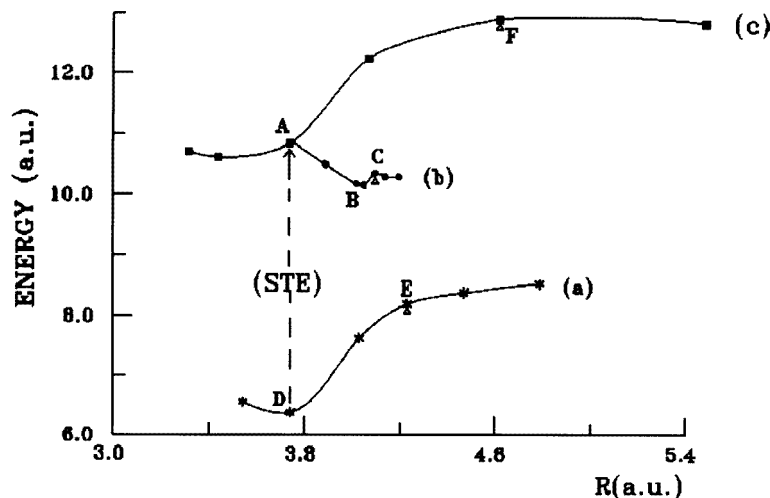


Figure 3. The adiabatic potential energy curve of the STE/FH pair. Curve (a): the ground state; curve (b): the hole excited state; and curve (c): the electron excited state. Points C, E, and F represent the positions at which the bond switching occurs on curves (a), (b), and (c) respectively. Point D on curve (a) represents the equilibrium configuration of the STE—the ground state. Point A represents its corresponding Franck–Condon excited state on curves (b) and (c).

Secondly, we performed calculations of the adiabatic energy curves of the STE/FH pair as functions of increasing F–H separation for the ground state, the electron excited state, and the hole excited state. The results are as shown in figure 3. In figure 3, point D represents the equilibrium configuration of the STE in the ground state. Point A corresponds to its Franck–Condon excited state. The conversion points E, C, and F at which the STE is converted to the F–H pair, are shown in figure 3 for each curve. The energy barriers against H-centre diffusion are taken as the energy difference between the energy at the A or D point and the energy at the corresponding conversion point. From our calculations, several conclusions can be summarized as follows.

(1) The energy barriers against H-centre diffusion in the ground state and the electron excited state of the STE are 2.00 eV and 2.10 eV, respectively. Thus, the thermally activated H-centre diffusion from the F centre cannot occur for these two states of the STE in MgF_2 .

(2) As shown by figure 3, curve (b), the excitation energy obtained from cascade excitation at point A is partly converted to lattice relaxation energy and partly to the kinetic energy of the H centre during the $A \rightarrow B$ relaxation process. It is difficult to estimate the amount of kinetic energy that the H centre at point B in figure 3 has, but, because the energy difference $\Delta E_{A \rightarrow B}$ is about 0.8 eV, and there is only a 0.16 eV energy barrier between B and C, there is a good likelihood of H-centre diffusion across a modest potential barrier.

After the H centre crosses the barrier, there is a fairly flat adiabatic energy curve. We therefore conclude that the F–H pairs are generated only by hole excitation of the STE. According to our calculation, a rotation of about 80° has been found, after which the STEs are converted to F–H pairs. The distance between the F centre and the H centre is about 4.0 au at the conversion point C.

(3) The hole excited state of the STEs can be reached by photoexcitation of the STE only at appropriate photon energies.

It is interesting to compare some differences between the ways in which stable F–H pairs are created in alkali halides and alkaline-earth fluorides, including MgF₂ studied here. In alkali halides of NaCl structure, there are close-packed rows of halogen ions, while such rows are absent in the alkaline-earth fluorides. In all ionic halides, the excited electron of a spin-triplet STE seems to split from the self-trapped hole, and localize as an F centre. When this occurs, the halogen molecular ion, at which the hole is localized, is expelled from its original site. A stable F–H pair is created if the H centre can be removed outside the range of recombination with the electron during the exciton lifetime. This is accomplished dynamically in many alkali halides even at 4 K, but all alkali halides also have a thermal channel. Theoretical calculations for these materials indicated that there is no significant energy barrier on the adiabatic potential energy curves of the triplet STE–(F–H) pair system. At the same time, an excitation of the triplet STE to either an electron or hole excited state also enhances the F-centre formation (the cascade experiment [7]). Electron excitation allows the STE to undergo a repeated off-centre dynamic process during the pulse duration [2], while hole excitation allows the hole to diffuse away as described above [23]. In all alkaline-earth fluorides, the dynamic F-centre creation yield is extremely low [4] under conventional ionizing irradiation, even though the off-centre relaxation is strong. The energy barrier shown in figure 3 for the lowest triplet STE state in MgF₂ explains this observation. On the other hand, this is certainly related to the absence of a close-packed row of fluoride ions in this lattice. Only when the hole is photoexcited to a non-bonding or anti-bonding state can the hole get away from the nearby F centre, and escape recombination. We note here that F–H pairs have been detected in BaFBr [24].

4. Conclusions

In this work, the STEs and F centres in MgF₂ are studied by means of the extended-ion method. We are primarily interested in two aspects of the defect in MgF₂. The first aspect concerns the structure and spectra. Our calculation shows that the STE is actually an off-centre nearest-neighbour F–H pair in the equilibrium configuration. The most favourable configuration among the four possible configurations of the STE is the one having C₁ symmetry. Theoretical results for the spectra of the F centre and STE are in good agreement with experiments. The more interesting aspect concerns the F–H pair formation mechanism; the stable F–H pairs are generated only in the hole excited state of the STEs under cascade excitation. A model of excited-hole hopping diffusion is proposed to explain the F–H pair formation. Hole excitation promotes an electron from the σ_g bonding orbital to the σ_μ antibonding orbital of the F₂⁻ pair, and opens up the possibility of hole hopping motion overcoming a modest potential barrier. A succession of a few similar hops of the hole centre could effectively take it away from the range of recombination, with the excited electron localized at the F centre, resulting in a stable F–H pair.

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