Ab initio modeling of radiation damage in MgF$_2$ crystals

F.U. Abuova [a], E.A. Kotomin [b,*], V.M. Lisitsyn [c], A.T. Akilbekov [a], S. Piskunov [b]

[a] *L. N. Gumilyov Eurasian National University, 3 Munaitpasova Str., Astana, Kazakhstan*
[b] *Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., LV-1063, Riga, Latvia*
[c] *Tomsk Polytechnic University, Tomsk 634003, Russia*

A R T I C L E   I N F O

A B S T R A C T

MgF$_2$ with a rutile structure is important radiation-resistant material with numerous applications due to its transparency from vacuum ultraviolet to infrared range of photon energies. We present and discuss the results of calculations for basic radiation defects in this crystal. The study is based on the large scale *ab initio* DFT calculations using hybrid B3PW exchange–correlation functional and atomic basis set. We analyzed the electronic structure, atomic displacements, charge density distribution as well as defect formation energies using large supercells. We compared properties of close and well separated F–H (Frenkel) defect pairs as well as individual defects. We simulated also formation and energetic preference of inert F$_2$ interstitial molecules as sinks of mobile interstitial fluorine atoms which is relevant for material radiation stability. We discussed also diffusion of the primary electronic defects—F centers.

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1. Introduction

Optical devices (e.g. lenses and windows) made of magnesium fluoride (MgF$_2$) are transparent over an extremely wide range of photon energies, from vacuum ultraviolet to infrared. Its another advantage is high radiation stability: concentrations of *stable* radiation defects therein are 3–5 orders of magnitude smaller than in alkali halide crystals. On the other hand, production efficiency of primary Frenkel defects—F and H centers—is close to that in alkali halides and constitutes about 100 eV [1–4]. This means that most of radiation-induced defects rapidly recombine. The reason for this could be lack of deep traps for mobile H centers in MgF$_2$, such as cation vacancies in alkali halides. Indeed, according to different estimates, the formation energies of Frenkel and Schottky defects in cation sublattice in MgF$_2$ are 7.7–17 eV and 6.3–7.4 eV, respectively, i.e. much larger than in alkali halides (2–4 eV and 1.4–2.7 eV, respectively). The fact that the F centers are still accumulated in MgF$_2$ means that a small fraction of the complementary H centers is transformed into more stable immobile hole centers. This is supported by the fact that no *H* centers are observed in irradiated MgF$_2$ crystals, even at low temperatures. It could be logical to assume that such complex hole centers are products of the encounter of the two mobile interstitial fluorine atoms — F$_2$ neutral molecules in interstitials positions [5]. This idea is also supported by an increase of the efficiency of radiation defect accumulation after MgF$_2$ doping with trivalent rare-earth ions which are compensated by interstitial fluorine ions [5].

Such F$_2$ molecules are optically nonactive, not paramagnetic and thus hardly could be detected experimentally, unlike complex hole centers, X$_3^-$ molecules well studied in alkali halides. Formation of such highly stable immobile molecules could explain the fact that processes of a mutual transformation of the electronic color centers in irradiated MgF$_2$ crystals occur similarly to those in additively colored crystals, e.g. photo- and photo-thermal F ↔ F$_2$ center transformation occur without any reduction of the electronic center concentrations [1].

It is important to check the above-presented hypothesis theoretically, in order to understand at the atomistic level the reasons of MgF$_2$ high radiation stability. Despite several *ab initio* calculations of basic MgF$_2$ properties (both bulk [6–8] and surfaces [9,10]), we are not familiar with defect studies in this material at the *ab initio* level. Recently we performed first calculations for the F [11] and H [12,13] centers (interstitial fluorine F$_2^-$ molecules) therein.

In this paper, we present main results of the *ab initio* calculations of several types of Frenkel defect pairs in the MgF$_2$ bulk.

2. Method of calculations

MgF$_2$ (rutile) has a tetragonal *P*4$_2$/mnm structure with two formula units in the unit cell. As in previous calculations on the MgF$_2$ bulk and (001) surface [9–13], we used here the CRYSTAL computer code [14] using localized, Gaussian-type basis sets. The

spin-polarized calculations were performed using the DFT−HF hybrid exchange–correlation B3PW functional [15] which gives better agreement of calculated and experimental MgF$_2$ optical gap than other functionals (9.5 eV (B3PW) vs 19.65 eV (HF), 6.9 eV (GGA-PBE), compare with the experimental value of 12.5 eV [9]).

The reciprocal space integration was performed by sampling the Brillouin zone with $5 \times 5 \times 5$ Pack–Monkhorst mesh [16]. To achieve high accuracy, large enough tolerances of 7, 8, 7, 7, and 14 were chosen for the Coulomb overlap, Coulomb penetration, exchange overlap, first exchange pseudo-overlap, and second exchange pseudo-overlap integrals, respectively [14]. In calculations we applied the basis set developed by Catti et al. for the F atom [17] and by McCarthy and Harrison [18] for the Mg atom. The effective atomic charges were calculated using the Mulliken population analysis [14].

The obtained atomic charges (−0.90 e for F and 1.8 e for Mg) confirm ionic nature of the chemical bonding. In calculations we used $2 \times 2 \times 2$ times expanded 6-atom rutile unit cell (3% defect concentration). As a result, we obtained the relaxed lattice geometry, effective atomic charges, atomic spins, chemical bond populations, the band structure, density of states (DOS) and defect formation energies. In order to get an accurate description of the F center, an extra basis set has been centred in the fluorine vacancy, corresponding to the *ghost* atom. For the *ghost* atom, we used the same basis set as that used for the F$^-$ ions of the bulk MgF$_2$.

We calculated several types of the Frenkel defects: close F−H pairs, well-separated pairs (both shown schematically in Fig. 1) where the *H* centers were oriented along either the (0 0 1) or (1 1 0) directions as well as formation of interstitial F$_2$ molecules (Fig. 2). Our previous study of the isolated H centers shows [12,13] that the defect (1 1 0) orientation is energetically more favourable. Note that despite a whole supercell is neutral, the effective charges of oppositely charged defects (F−H centers) and other ions are calculated in a self-consistent way.

3. Main results

3.1. Frenkel defects

As is well known, the primary radiation defects are Frenkel pairs of fluorine vacancies with trapped electrons (F centers) and interstitial fluorine atoms which rapidly form the diatomic F$_2^-$ molecules (called the H centers) with a regular F$^-$ ion. The formation energy of the close Frenkel pair shown in Fig. 1 is 8.36 eV. The distance between the F and H centers here is 1.85 Å only. The interatomic distance within the H center (diatomic molecule) is 1.87 Å, considerably smaller than in the free H center [12,13]—1.96 Å. This is caused by a strong mutual defect perturbation.

The formation energy of the well separated (and stable) F−H pair is larger by 0.2 eV. The distance between defects was here as large as 4.8 Å. As a result, the interatomic distance within the H center becomes practically the same as in the isolated defect. The Frenkel pair formation energy in this case almost coincides with the sum of the formation energies of the two individual defects.
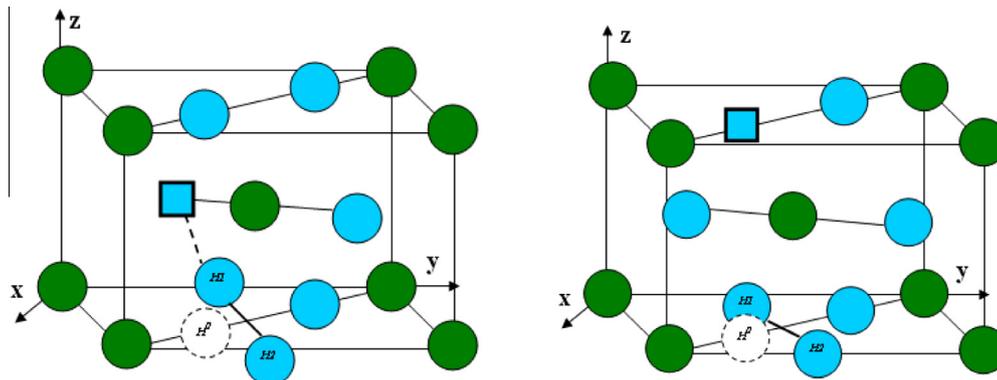

Fig. 1. The nearest (left) and well separated (right) F−H (1 1 0) pairs in MgF$_2$. Blue (light) atoms are fluorine ions, green (dark) magnesium ions. Dotted circle indicates position of a regular fluorite ion before the H center formation. The F center is marked as a square, the H center consists of the H1 and H2 ions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
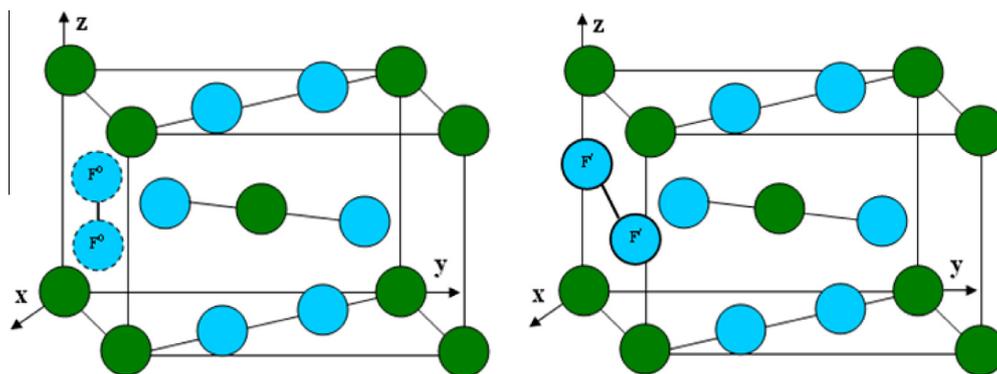

Fig. 2. The initial (left) and optimized (right) configurations of interstitial F$_2$ molecule.

Table 1
The effective charges Q (e), magnetic moments S (μ_B) on the two fluorine ions constituting the H centers with two possible orientations and defect formation energies (eV).

Atoms	Q	S	E_f	Q	S	E_f
(001)			3.3	(110)		3.6
H1	−0.46	0.47		−0.77	0.23	
H2	−0.46	0.47		−0.31	0.62	

The formation energy of another type of the Frenkel defects– with the H center (001) orientation— is energetically considerably (≈ 3 eV) less favorable. This confirms mentioned above trend observed by us [12,13] for the single H centers.

Table 1 shows the atomic effective charges within a close Frenkel pair (Fig. 1). As one can see, charges of the H1 and H2 atoms forming the (110)-oriented H center are not identical, similarly to the free H center anisotropy [12]. Their total spin is close to the unity, confirming the F_2^- model of the paramagnetic defect. The same is true for the F center; vacancy traps nearly one electron. Only the charges of several nearest to defect Mg ions deviate more than by 0.1 e from those in the perfect crystal. This shows that the Frenkel pair produces only a local perturbation of the charge distribution. The analysis of coordinates of atoms surrounding the F–H pair shows that the largest displacements correspond to the fluorine ions H1 and (less) H2 forming the H (110) center. (The anisotropy in their displacements was discussed in Ref. [12].) However, several nearest F⁻ and Mg ions are also considerably displaced, despite their charges are only slightly perturbed. The formation energies in Table 1 give the energy gain due to transformation of an interstitial F atom into diatomic molecule (H center). One can see effect of considerable chemical bonding within the H center.

The electronic density map for a close F–H pair (Fig. 3) confirms strong anisotropy of the charges in the hole center and their strong mutual perturbation. Note that only ions nearest to the pair are slightly perturbed.

3.2. Complex hole center

As discussed in Section 1, we simulated formation of the neutral and inert F_2 molecule as a result of the reaction between two interstitial fluorine atoms. We studied its several possible spatial configurations and found that the F_2 molecule has lowest energy and fits quite well into the rutile structure in the face-center position (Fig. 2). Its formation is energetically more favorable (by 1.3 eV) than the pair of the two separated fluorine interstitials. The optimized F–F distance in this molecule is 1.59 Å, i.e. larger by $\approx 10\%$ then that in a free molecule. The formation of such inert and immobile F_2 molecules prevents the F–H center recombination and thus allows accumulation of stable F centers. Since the probability of meeting two mobile interstitials is quite low due to their fast transformation into the H centers, concentration of stable F centers should be also small, in agreement with the experimental data [1].

3.3. F center diffusion

The efficiency of the primary radiation defect recombination is controlled by defect diffusion. We performed calculations of the energy barriers for four kinds of the F center jumps in the rutile structure (Fig. 4): C_1, C_{2h}, D_{2h} and C_{2v} We performed these calculations for the two different exchange–correlation functionals: hybrid B3PW and GGA-type PBE. The energy differences for these functionals are typically 0.1–0.2 eV. Due to technical reasons, ghost functions were not centers at vacancy sites. As follows from Table 2, the most efficient is F center diffusion path with alternating C_1 and D_{2h} jumps which corresponds to the largest of these two energies (1.59 eV). There are no experimental data to check our prediction.
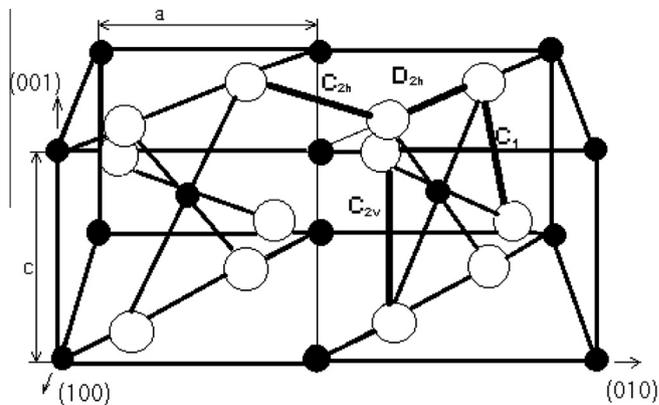

Fig. 4. Four possible jumps of fluorite vacancy in MgF$_2$ structure.
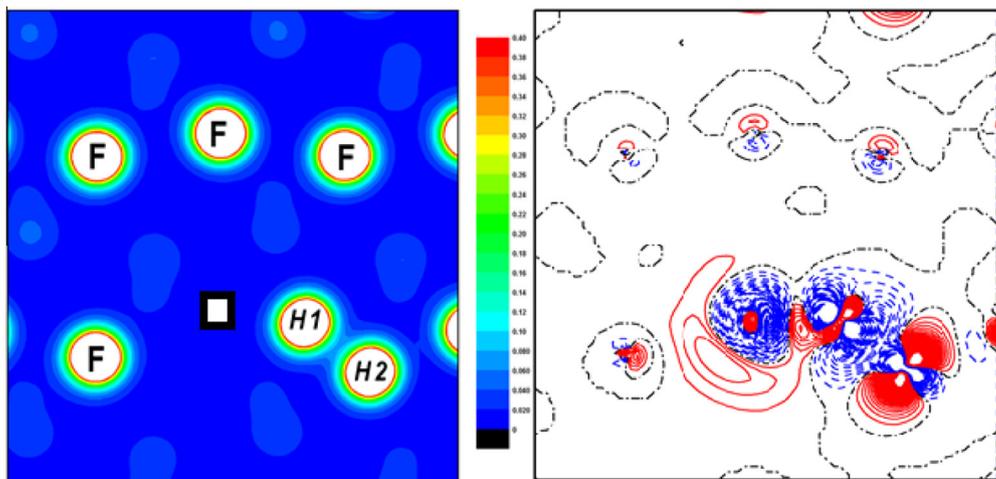

Fig. 3. The total (left) and difference (right) electronic density maps for the nearest F–H pair. The latter is the difference of a perfect crystal density and a sum of the densities of the defective crystal and an F atom in a vacancy position minus F atom in the interstitial position. Thus the difference density plot shows the charge redistribution caused by defects. Blue color (dashed lines) on the right panel corresponds to excess of electron density, red its deficiency. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
The migration energies (eV) for the F center in four possible directions.

Direction	Interatomic distance (Å)	B3PW (eV)	PBE (eV)
C_1	2.84	0.98	0.89
C_{2v}	3.02	1.13	1.32
D_{2h}	3.31	1.59	1.54
C_{2h}	3.36	1.72	1.65

The only previous theoretical study was performed long ago using the pair-potential method [19] which gave the migration energy of 1.53 eV and a very small energy for C1 jumps. Our calculations are more precise since the realistic electron density distribution and re-distribution at the saddle point of diffusion are taken into account. In particular, the effective charge of jumping fluorite ion is increased by 0.1 e compared to a regular fluorine ion. Note also recent *ab initio* calculations for the F centers in the two other fluorites: CaF_2 and BaF_2 where the obtained migration energies were 1.83 eV and 1.70 eV [20,21], respectively, close to our result.

4. Conclusions

Our *ab initio* calculations have shown that the formation energy of a well separated Frenkel pair in MgF_2 is 8.36 eV, accompanied with the H center (110) orientation. We have demonstrated also that it is energetically favorable for the two mobile interstitial fluorine atoms to form neutral and inert interstitial F_2 molecule. This could be a key for understanding MgF_2 high radiation stability. The diffusion energy for the primary F centers is found to be 1.6 eV. Detailed study of hole H center migration is in progress.

Acknowledgments

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