Stabilization of primary mobile radiation defects in MgF$_2$ crystals

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ABSTRACT

Non-radiative decay of the electronic excitations (excitons) into point defects (*F*–*H* pairs of Frenkel defects) is main radiation damage mechanism in many ionic (halide) solids. Typical time scale of the relaxation of the electronic excitation into a primary, short-lived defect pair is about 1–50 ps with the quantum yield up to 0.2–0.8. However, only a small fraction of these primary defects are spatially separated and survive after transformation into stable, long-lived defects. The survival probability (or stable defect accumulation efficiency) can differ by orders of magnitude, dependent on the material type; e.g. ~10% in alkali halides with f.c.c. or b.c.c. structure, 0.1% in rutile MgF$_2$ and <0.001% in fluorides MeF$_2$ (Me: Ca, Sr, Ba). The key factor determining accumulation of stable radiation defects is stabilization of primary defects, first of all, highly mobile hole *H* centers, through their transformation into more complex immobile defects. In this talk, we present the results of theoretical calculations of the migration energies of the *F* and *H* centers in poorly studied MgF$_2$ crystals with a focus on the *H* center stabilization in the form of the interstitial F$_2$ molecules which is supported by presented experimental data.

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1. Introduction

MgF$_2$, having a rutile structure, falls in the category of the alkaline earth (AE) fluorides of the group IIA of the periodic table which form highly ionic MF$_2$ salts with the fluorine ions, where M stands for the metal cation. Three other cations of the AEF in this group are Ca, Sr and Ba. The latter three cations form AE fluorides with the fluorite structure, while alkali fluorides (LiF, NaF, KF and RbF) form NaCl-type (f.c.c.) structure, except for CsF having CsCl lattice type. Table 1 contains summary of optical absorption bands of the most important radiation point defects in LiF, alkaline earth fluorides and MgF$_2$ [1–3].

Magnesium fluoride (MgF$_2$) is highly transparent over an extremely wide range of photon energies, ranging from vacuum ultraviolet to infrared and thus has found a lot of applications in the different optical devices (e.g. lenses, filter, windows, laser elements) [4]. Many applications are related to its high radiation stability.

Non-radiative decay of the electronic excitations (excitons) into point defects (vacancy-interstitial pairs called the *F*–*H* pairs of

Frenkel defects) is main radiation damage mechanism in many ionic (halide) solids [5,6]. Typical time scale of the relaxation of the electronic excitation into a primary, short-lived defect pair is about 1–50 ps with the quantum yield up to 0.2–0.8. However, only a small fraction of these close primary defects could spatially separate [7–11] and survive thus transforming into stable, long-lived defects. The survival probability (or stable defect accumulation efficiency) can differ by orders of magnitude, dependent on the material type; e.g. ~10% in alkali halides with f.c.c. or b.c.c. structure, 0.1% in rutile MgF$_2$ and <0.001% in fluorides MeF$_2$ (Me: Ca, Sr, Ba) [12,13].

The key factor determining accumulation of stable radiation defects is immobilization of primary defects, first of all, highly mobile hole *H* centers, through their transformation into more complex defects, which prevents their annihilation with complementary *F* centers. In alkali halides these aggregation processes are well studied [14–18], mobile (typically already above 50 K) *H* centers upon encounter are transformed into *V*-type centers: X$_3^-$ molecular ions occupying two anion and one cation lattice sites (X stands for halogen = F, Cl, Br). The necessary (pre-irradiation type) cation vacancies exist due to relative low Schottky defect formation in alkali halides which results in efficient formation of the *V*-type complex hole centers. Cation vacancies in alkali halides are

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Table 1
The band gaps and positions of the absorption band maxima for the V_k, H and F-type defects in fluorides.

	LiF	CaF$_2$	SrF$_2$	BaF$_2$	MgF$_2$
Eg (eV)	13.6	11.5	10.8	10.3	13.0
V_k (nm)	348	320	326	336	302 (?)[*]
H (nm)	310	314, 285	325	364	288 (?)[*]
F (nm)	250	366–375	449	606	250–260
		521			
F_2 (nm)	444	366	427	550	219
		521			317
					369
					403
Intrinsic colloids (nm)	450	540–560	550–600	400–450	280

[*] No experimental data are available on the positions of the V_k and H hole center bands in the absorption spectrum of MgF$_2$ crystal. The approximate value of the H-band maximum, obtained in [2] by extrapolation, is 4.3 eV and coincides with the maximum of absorption by the neutral molecule [22] and the maximum of the transient self-trapped exciton absorption band.

also created by radiation [14] or as a charge compensators in impurity-vacancy dipoles [19].

However, this is not the case for MeF$_2$ where formation energy of Schottky defects and Frenkel pairs in cation sublattice is larger than of anion Frenkel pairs. 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) [20]. This prevents contribution of cation defects into V-type defect formation and thus hole defect stabilization similar to the alkali halides. As a result, most of the H centers recombine with the complementary F centers, only a fraction of the F centers (and thus, H-related centers) still survives and accumulates. It was suggested [21]] that pairs of the holes F^0 upon encounter form interstitial F$_2$ molecules containing no cation defects. Such immobile molecules are not detectable optically, have large binding energy (i.e. very stable upon annealing) and weakly interact with electrons. This could be a reason, why upon photo-thermal stimulation, electronic color centers in MgF$_2$ crystals behave similarly to the electronic centers in additively colored crystals [21].

VUV studies of MgF$_2$ [23] have suggested that thermo-activated migration of H centers occurs at about 80 K and results in their recombination with distant immobile F centers with appearance of self-trapped exciton luminescence TSL peak at 82 K (with heating rate 10°K/min). Much earlier, similar annealing stage at 60 K with corresponding activation energy 0.17 eV has been observed in thermal neutron irradiated MgF$_2$ [24]. In their next paper it was proposed that this stage at 60 K possibly arises due to migration of H centers [25]. As for the F centers in MgF$_2$, it was reported that they are stable at least up to 500 K [26,27].

The purpose of this paper is to calculate mobility of the F centers in MgF$_2$ and to check hypothesis [21] on the mobile interstitial aggregation with formation of the F$_2$ interstitial molecules.

2. *F* center diffusion in MgF$_2$

The migration energy of primary F centers was calculated using two different *ab initio* approaches, based on the atomic basis sets and plane waves, respectively. The barrier energies in four possible directions, charge redistributions and atomic displacements at the saddle point of fluorine ion migration were calculated and compared. First of all, the CRYSTAL computer code [28] using localized, Gaussian-type basis sets was used. The spin-polarized calculations were performed using the DFT-HF hybrid exchange–correlation B3PW and generalized gradient approximation PBE

exchange–correlation functional [29,30] which gives better agreement of calculated and experimental MgF$_2$ optical gap than other functionals.

For a comparison, first principles calculations using an alternative basis set of plane waves (VASP 4.6 spin-polarized computer code [31]) were also performed. The projector augmented wave (PAW) [32] method together with the ultra-soft pseudopotentials combined with the non-local exchange–correlation functional (PBE) within generalized gradient approximation (the same as used in the CRYSTAL calculations) have been used and compared with a standard Local Density Approximation (LDA). The cut-off energy in plane wave calculations was fixed at 520 eV.

In the rutile crystalline structure shown in Fig. 1 four possible jumps of the F center are possible. The relevant calculated energies obtained using two above-described methods are summarized in Table 2. First of all, the lowest energy corresponds to C$_1$ jumps, around 1 eV in CRYSTAL and 1.5 eV in VASP calculations (we compare results for the same PBE functional). However, three-dimensional vacancy motion needs a combination of the C$_1$ jumps with others, e.g. D$_{2h}$ which needs a larger energy (1.5 eV and 1.7 eV, respectively). Thus, the effective 3D migration energy is expected to be limited by the D$_{2h}$ jumps. The results of the CRYSTAL calculations for two different functionals are quite similar, whereas those with the same PBE functional but two different computer codes shows essentially larger energies in the plane wave calculations (to be discussed below). The VASP-LDA energies are closer to the CRYSTAL results than the VASP-PBE, despite the latter are considered as more accurate.

For a comparison, we added also the results of calculations based on inter-atomic potentials [33]. These energies are much smaller and qualitatively differ from first-principles calculations. In particular, the energy for C$_1$ jumps is predicted to be so low that defects should be mobile even at liquid nitrogen temperature what contradicts the experimental data.

Summing up, our first principles calculations predict that 3D migration of the F centers in MgF$_2$ crystals needs the effective activation energy of 1.5 eV. This value is close to typical energies for the F center diffusion in other alkali halides and certainly smaller
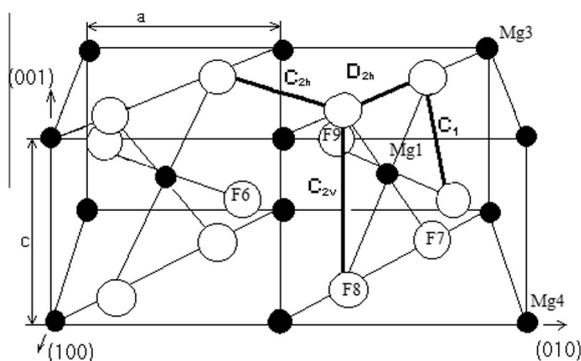

Fig. 1. The schematic view of a rutile structure and four types of F vacancy jumps therein.

Table 2
Calculated barrier energies (eV) for four different types of fluorine vacancy jumps.

Direction/jump distance (Å)	Interatomic potentials [33]	Crystal (B3PW)	Crystal (PBE)	VASP (PBE)	VASP (LDA)
C$_1$ (2.84)	0.03	0.98	0.89	1.55	1.12
C$_{2v}$ (3.02)	1.53	1.13	1.32	1.57	1.27
D$_{2h}$ (3.31)	0.31	1.59	1.54	1.72	1.52
C$_{2h}$ (3.36)		1.72	1.65	2.19	1.91

Table 3
Summary of the activation energies for F-type center diffusion energies in ionic solids.

Crystal	Defect	Expt	Theoretical	References
KCl	F center	1.35–1.65	1.64	[34]
MgO	F^+ center		2.72	[35–39]
	F center	3.4	3.13	
CaF$_2$	F center		1.69	[40]
MgF$_2$	F center		1.50–1.72	this work

than in MgO, as shown in Table 3. Such quite high migration energies show that the F centers in MgF$_2$ should be practically immobile at moderate temperatures, in agreement with experiments [26,27].

Thus, we conclude that high radiation resistance of MgF$_2$ is not related to the F center migration but likely to secondary processes (e.g. H center aggregation peculiarities as was studied in details in the case of alkali halides [14,15,41,42]). Note here that aggregates of H centers in fluorides show absorption bands in VUV spectral range [41,43]. In particular, in LiF, Mayhugh and Christy have observed that optical absorption band is produced at 113 nm (11.0 eV) in both pure and Mg-doped LiF by irradiation with X rays at room temperature [43]. This band, which appears to be intrinsic like the F band, was identified as the so-called V_3 band. Its peak-wavelength position follows the same dependence on anion radius as has been found previously for alkali chlorides, bromides, and iodides. Later Lushchik et al. [41] have found a similar band at 10.5–11.8 eV connected with F_3^- molecules. According to their model, the stabilization of interstitials up to 550–620 K in LiF irradiated at room temperature occurs by association of an H center with a V_K center (a self-trapped hole) or a hole localized near v_c (i.e. near a V_F center) and a subsequent formation of a trifluorine F_3^- molecule. However, this mechanism cannot be easily generalized for rutile-structured MgF$_2$ crystals, where no self-trapping holes were observed. Thus, other mechanisms should be considered for explanation of the interstitial stabilization, which will be described below.

3. Theoretical modeling of interstitial fluorine molecule

Based on recent first principles modeling of the H centers in MgF$_2$ [44], and in agreement with experiments [45,46], it was found that the (110) oriented H centers are energetically more favourable in MgF$_2$ than the (001) oriented. Further step was to simulate the aggregate of two H centers formed upon their mutual approach. We checked a hypothesis [21,47] that a neutral and inert interstitial F$_2$ molecule could be created as a result of the reaction between two interstitial fluorine atoms F^0 before they were transformed into the H centers. We have analyzed several possible

spatial configurations and found that the hypothetical F$_2$ molecule has lowest energy and fits quite well into the rutile structure in the face-center position (as shown in Fig 2). The optimized F–F distance in this molecule is 1.59 Å, i.e. larger by $\approx$10% then that in a free molecule. Its formation is energetically more favorable (by 1.3 eV) than the pair of the two separated fluorine interstitials. The formation of such inert and immobile F$_2$ molecules prevents the F–H center recombination as well as possible recombination with charge carriers (electrons and holes, created by radiation), what thus promotes the survival and creation of stable F centers. Since the probability of the collision of 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 [8,9].

Similar situation have been also considered in CaF$_2$ crystals doped with trivalent rare-earth ions (Sm^{3+} and Ho^{3+}), which are compensated by interstitial fluorine ions [21]. In particular, thermal stability of the radiation defects (F-type) produced at room temperature depends on both irradiation dose and impurity concentration. It was suggested and confirmed by computer modelling, that the results obtained can be described by the existence of two stable hole centers, namely fluorine atom F^0 and molecules of fluorine (F$_2^0$) in the interstices. Changing the ratio in favor of the hole centers F$_2^0$ with increasing of the dose will increase the thermal stability of F-type centers. Note that the formation of the fluorine molecule from two atoms has the energy gain of 1.5 eV.

The formation of neutral F$_2$ molecules (including their weak interaction with the electron–hole pairs) is supported by the following experiment on the $M \rightarrow F$ electron center transformation (M is a dimer of two nearest F centers). Such radiation-induced conversion has been performed by us under electron irradiation with the energy of 1.2 MeV. In the beginning of the experiment, the F and M centers were created in MgF$_2$ at room temperature, and then by optical and thermal treatment all defects were transformed into M (C$_{2h}$-oriented) centers. Further electron irradiation of MgF$_2$, containing these non-equilibrium dimer centers in the temperature range 290–500 K leads to their transformation into single F-centers (Fig. 3). This process has the following properties:

1. It can be described by the first-order reaction, as shown in Figs. 3 and 4; $dn_M/dt = -K\, n_M$.
2. In this process the total electron defect concentration $n_F + 2n_M$ is constant and equals $2n_M(0)$.
3. In this transformation process, only electron F and M centers are observed.
4. $M \rightarrow F$ electron center transformation occurs due to interaction with irradiation-induced hole H centers: $M + H \rightarrow F$.
5. The $M \rightarrow F$ center transformation is characterized by the activation energy of 0.12 eV at $T > 415$ K and 0.37 eV at $T < 390$ K.
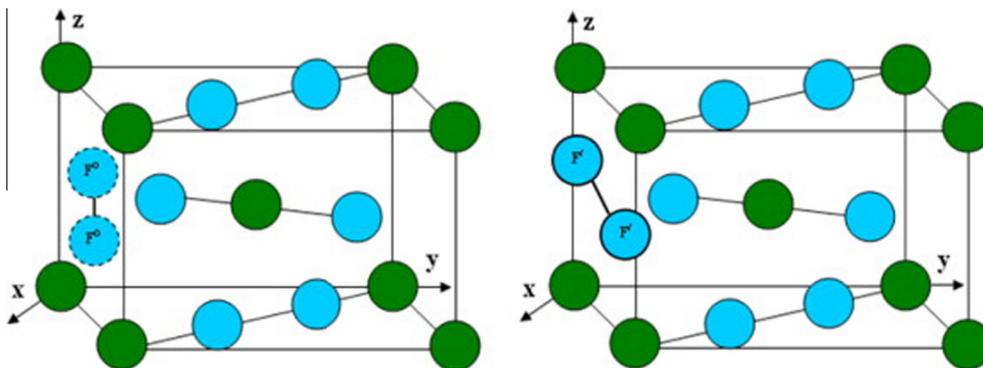

Fig. 2. The initial (left) and optimized (right) configurations of interstitial F$_2$ molecule in a rutile structure.
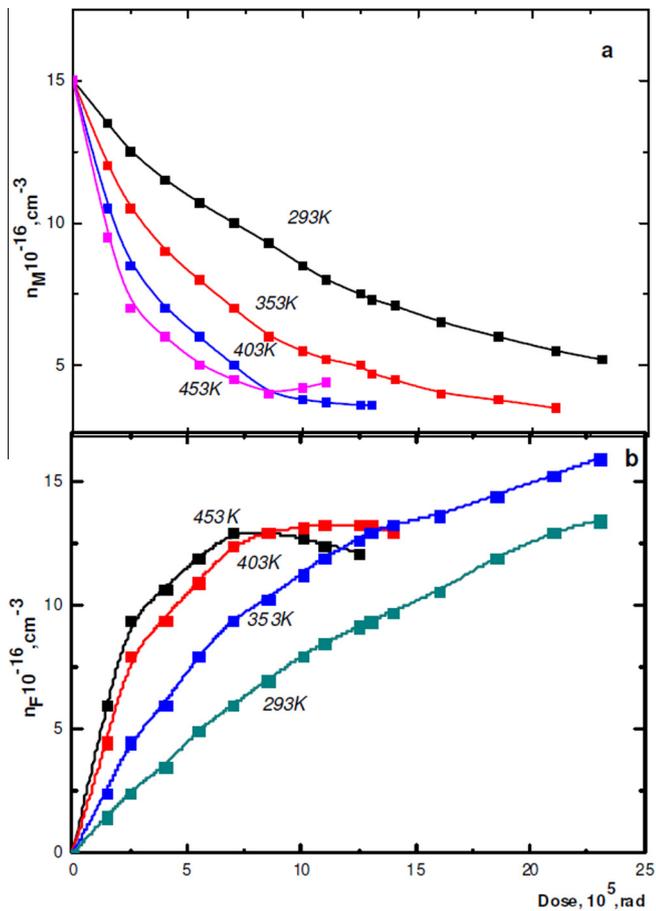
Fig. 3. Dose dependence of the number of the *M* center (a) and *F* center (b) under electron irradiation (1.2 MeV) of MgF$_2$, containing only pre-irradiation *M*-type centers at different temperatures.
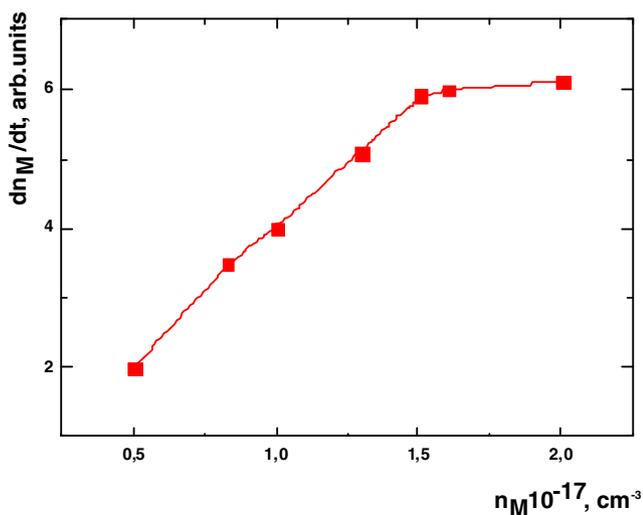

Fig. 4. Dependence of the destruction rate of *M* centers on the initial *M*-center concentration in MgF$_2$ crystals, with preliminary oriented *M*-centers, irradiated by 1.2 MeV electrons at room temperature.

It is important to note here that although MgF$_2$ crystal contains also some hole centers (it is impossible to create by irradiation only electron centers), these hole centers do not manifest themselves. The latter fact gives a strong support to their neutral charge and thus, weak interaction with electrons and *H* centers. Note that this situation strongly differs from irradiated alkali halides [48] but reminds the case of additively-colored alkali halides [49,50].

4. Conclusions

By means of the first principles electronic structure calculations, the migration of the primary *F* centers in rutile MgF$_2$ crystal was studied. Its migration energy is estimated 1.5 eV, much larger than the *H* centers which thus are much more mobile. (Accurate calculations of the *H* center migration energy are in progress.) It is shown that the key for understanding radiation stability of MgF$_2$ crystals lies in stabilization of primary mobile hole *H* centers in the form of interstitial neutral di-fluorine F$_2$ molecules, unlike X$_3^-$ complex hole centers in alkali halides occupying three lattice sites. This explains also peculiarities of the experimental observation of photo-thermal transformation of the electronic centers in electron-irradiated MgF$_2$.

Acknowledgements

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