

# Accumulation Dynamics of Radiation Defects in MgF<sub>2</sub> Crystals

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**Abstract** – The method of pulse optical spectrometry in a temperature range 12.5-500 K was used to study the regularities of *F*, *H*-pairs evolution in MgF<sub>2</sub> crystals. The research showed that Frenkel pair generation occurs from pre-defective mode. Pairs separated at more large distances at the stage of the initial distribution formation function are involved in *F*-centers accumulation. The *F*- and *H*-centers separation results in *H*-center shift at  $T < 180$  K due to excessive electron excitation energy. The probability of the extended function formation of initial distribution grows at  $T > 180$  K due to thermal energy. It makes the probability of *F*- and *H*-centers separation increase when temperature increases. Since the efficiency of *H*-center transformation into a stable hole center at 250 K is low, the main part of separated *H*-centers recombines with *F*-centers. The relaxation kinetics of *F*-center absorption in MgF<sub>2</sub> is limited by recombination processes occurring in close pairs at any temperature.

## 1. Introduction

The basic stages of radiation defects (color centers) accumulation in ionic combinations with a weak formation mechanism are as follows: generation of Frenkel pairs (*F*, *H*-pairs), spatial separation of pair components, and their transformation into steady color centers. As an alternative to *F*, *H*-pairs creation at low temperatures, there is a singlet-triplet excitons (STE) formation. The aim of the research is to determine basic processes at each stage of primary radiation defect accumulation in MgF<sub>2</sub> crystals being irradiated by electron in the temperature range from 12.5 to 500 K. A pulse optical spectrometer with the following parameters was used in the study: spectral measurement region – 200-1200 nm; time resolution – 7 ns; measurement temperature range – 12.5-700 K; current pulse duration of nanosecond electron beam – 2-10 ns; electron beam current density – 0,1-1000 A/cm<sup>2</sup>; the maximum electron energy – up to 400 keV.

## 2. Primary Defect Generation in MgF<sub>2</sub>

STEs are created in MgF<sub>2</sub> mainly at 30 K. Their luminescence spectrum represents the 3.2 eV band. Luminescence decay kinetics after the pulse electron excitation is represented by the sum of exponents with the constants  $\tau_1 = 6.4$  ms и  $\tau_2 = 0.75$ . The STE absorption spectrum in MgF<sub>2</sub> consists of overlapping Gaussian bands with the maximum values being 4.3 eV, 4.7 eV, 5.15 eV, and 5.6 eV. At radiation transition 3.2 eV, there is a large Stokes shift (9 eV); STE absorption spectrum is found within the ultraviolet spectral re-

gion. The temperature of the STE emission quenching start (50-60 K) coincides with *H*-centers delocalization temperature. These and other facts [1 – 4] justify that STE absorption is caused by triplet-triplet (T-T) transitions with off-center nuclear configuration, its axis does not coincide with crystallographic directions of the crystal.

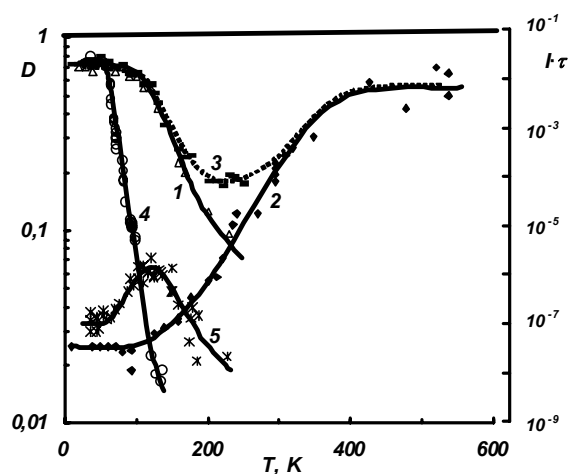


Fig. 1. Temperature dependences of the absorbance induced during a nanosecond electron beam pulse in maxima of STE absorption bands (1), *F*-centers (2), their sum (3) and light sums  $S_{3,2}$  (4) and  $S_{4,2}$  (5) 3.2 eV and 4.2 eV emission bands in MgF<sub>2</sub>

At low temperatures, a new luminescence 4.2 eV band with  $\tau_3 = 0.008$  ms [4] has been found. The growth of peak intensity  $I_0$  (measured at the moment of maximum intensity after electron pulse excitation) and the light sum ( $S_{4,2} = I_0 \tau$ ) of 4.2 eV band in the interval 60 – 110 K are followed by the reduction of  $S_{3,2}$  and  $I_0$  of 3.2 eV band. The reduction of  $S_{4,2}$  light sum at 110 K is followed by the reduction of STE concentration (Fig. 1, curves 4, 5). Therefore, the 4.2 eV band should be referred to STE, only with on-center configuration.

Temperature dependences of optical density in the maximum of 4.3 eV band of STE and *F*-centers absorption ( $D_{STE}$  and  $D_F$ ), induced during a pulse, are shown in Fig. 1 (curves 1 and 2). They correspond to the formation efficiency of the primary defects in MgF<sub>2</sub>. This research [3 – 5] as well as the data obtained by other authors suggests that energy spent on STEs generation at low temperatures makes  $\sim 2E_g$ , and the part of the created *F*-centers does not exceed 2–3 % of STEs. In the temperature interval 12.5 – 110 K, the number of *F*-centers formed during a nanosecond

electron beam pulse is constant (athermic generation area). At  $T > 120$  K,  $D_{STE}$  decreases, while  $D_F$  grows (the  $F$ -center thermosetting generation area); at  $T > 400$  K, it gets saturated. The energy spent on  $F$ -centers formation is  $\sim 2E_g$  at 500 K. The activation energy of exciton destruction and  $F$ -centers creation processes within 140–300 K is identical (0.07 eV) and it differs from STE emission quenching activation energy.

Thus, in the region of  $H$ -centers movement activation ( $T > 50$ ) STE emission quenching occurs, but it is not connected with transformation of an exciton into a  $F, H$ -pair. This experimentally proves that in  $MgF_2$   $F, H$ -pairs are created mainly (unlike alkali halide crystals) from a pre-defective state. STEs are formed under the same condition.

The scheme of the generation mechanism is presented in Fig. 2. At low temperatures, the electron excitation is created in the  $(e^- + p^+)$  state. The thermal energy is not sufficient enough to surmount the 0.07 eV barrier to transfer into  $(e^- + V_k^*)$  state which can cause  $F, H$ -pairs formation; the off-center STE with  $\pi - 3.2$  eV emission band. At 50 K, the STE nucleus can be transformed to another position of the lattice. However, in  $MgF_2$ , the barrier separating STE nucleus states and close  $F, H$ -pairs is high. Therefore, at these temperatures, only thermal quenching of excitons occurs. This explains the gap of temperature dependence of the  $D_{STE} + D_F$  total optical density (Fig. 1, curve 3). However, off-center STEs can be partially (the efficiency being very low) transformed into on-center configuration (4.2 eV band). At  $T > 110$  K, the transformation from  $(e^- + p^+)$  state into  $(e^- + V_k^*)$  state is possible. It leads to the growth of  $F$ -centers creation efficiency when temperature increases.

### 3. Accumulation of $F$ -centers in $MgF_2$ Crystals

Most of primary defects created in ionic crystals destruct at any temperature, part of them is transformed into stable color centers. The amount of stable  $F$ -centers in  $MgF_2$  crystals at all temperatures is less than that in alkali halide crystals with the same absorbed radiation dose. This can be seen when compared the accumulation efficiency of the  $F$ -centers in  $MgF_2$  and  $LiF$  [5]. In both materials, mainly STEs are created at low temperatures; whereas at high temperatures –  $F$ -centers. Radiation  $T \rightarrow S_0$  transition of off-type STEs in  $LiF$  (4.4 eV) and  $MgF_2$  (3.2 eV) have close values of Stokes-shift (8.68 eV and 9 eV); their values of emission quenching beginning temperatures are also close and they coincide with  $H$ -centers delocalization temperature. Both crystals have close areas of athermic (20–100) and thermosetting ( $T > 100$  K) processes of  $F$ -centers creation. Both crystals have saturation areas of  $F$ -centers creation efficiency (300 K in  $LiF$  and 500 K in  $MgF_2$ ). The values of energy spent on creation of STEs at 12.5 K (30 eV in  $MgF_2$  and 20 eV in  $LiF$ ) and energy spent on creation of  $F$ -centers at the satu-

ration stage at  $T > 400$  K are also close; temperature dependences of  $F$ -centers accumulation efficiency are similar.

The basic differences of defect formation and accumulation processes in  $LiF$  and  $MgF_2$ .

In  $MgF_2$  at  $T < 60$  K mainly STEs of the off-center type are formed, whereas in  $LiF$  mainly STEs of the on-center type are created. In  $MgF_2$ ,  $F, H$ -pairs are formed from a pre-defective state. In the range of 12.5–60 K, energy spent on the formation and accumulation of one  $F$ -center differs by one order (formation:  $2 \cdot 10^2$  eV for  $LiF$  and  $2 \cdot 10^3$  eV for  $MgF_2$ , accumulation:  $3 \cdot 10^3$  eV for  $LiF$ ,  $10^5$  eV for  $MgF_2$ ). At high temperatures, energy spent on  $F$ -centers formation is close, but  $F$ -centers survival efficiency differs a lot (percentage of accumulated ones vs the created ones): in  $LiF$  – about 20 %, at 300 K whereas for  $F$ -centers – 0.1 % at 500 K.

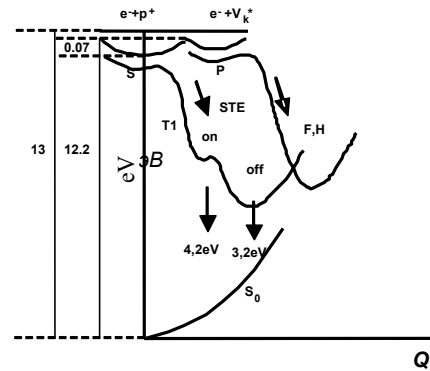


Fig. 2. Diagram of electron excitation relaxation in  $MgF_2$  crystal

The results obtained show, that principal causes of low efficiency of  $F$ -centers accumulation in  $MgF_2$  at  $T < 110$  is low efficiency of their generation, and high efficiency of  $F$ -centers accumulation is caused by low efficiency of a survival. It should be noted that at low temperatures in  $MgF_2$   $F$ -centers survive also less than in  $LiF$ .  $F, H$ -pairs formation in  $MgF_2$  at low temperatures is limited by the alternative channel existence of STE formation. Consider the reason of low efficiency of the  $F$ -centers survival in  $MgF_2$ .

Temperature dependence of the stable  $F$ -centers accumulation in  $MgF_2$  is typical for ionic crystals type, as different authors say and our data also have proved it (Fig. 3). The number of accumulated  $F$ -centers reduces sharply in  $H$ -centers delocalization area (50–60 K) and increases at  $T > 180$  K, getting its saturation at 250 K.

Annihilation of created Frenkel pairs can occur before their separation in space (correlated pairs), or after separation and the subsequent thermosetting  $H$ -center movement (not correlated pairs). The probability of accumulation is equal to  $P_{accum}(T) = P_{gen.}(T) \cdot P_{div.}(T) \cdot P_{stable}(T)$ . Therefore, the survival efficiency can be limited by either the probability of spa-

tial separation of  $F$ ,  $H$ -pairs components ( $P_{div}(T)$ ), or probability of the  $H$ -center transformation in the stable hole center of ( $P_{stable}(T)$ ) after separation. The efficiency ratio of these accumulation stages depends on this crystal temperature.

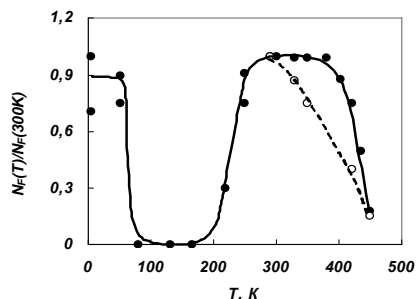


Fig. 3. Temperature dependence of  $F$ -centers accumulation efficiency in  $MgF_2$ . The dotted curve represents  $F$ -centers accumulation without their coagulation

### 3.1. $F, H$ -Pairs Separation in $MgF_2$ Crystals

The temperature dependence of non-equilibrium at this temperature  $H$ -centers which are effective traps for  $H$ -centers according to the following reaction:  $(F, H)_p + F_2 \rightarrow F_p + H_p + F_2 \rightarrow F_p + (H_p + F_2) \rightarrow F + F$  corresponds to the temperature dependence of formation efficiency of spatially separated  $F$ - and  $H$ -centers ( $P_{gen}(T)P_{div}(T)$ ) at  $T > 180$  K. This dependence for  $MgF_2$  is presented in Fig. 4. It was found to correlate with  $F$ -centers accumulation efficiency (activation energy of both processes – 0.12 eV) and not to correlate with  $P_{gen}(T)$   $F$ -centers generation efficiency. It means that  $F$ - and  $H$ -centers accumulation and separation are limited by one common process – the probability of  $P_{div}(T)$  spatial separation. Thus, the growth of survival efficiency in the range 180 – 250 K is caused by the increase of  $F$ ,  $H$ -pairs components spatial separation efficiency.

This curve illustrates that in the range of temperatures  $T < 180$  K, no  $F, H$ -pairs thermosetting spatial separation in  $MgF_2$  occur. In this case  $F$ -centers can survive only when originated pairs are located at more than the most close distance from each other, and  $H$ -centers are not mobile at this temperature. This case is represented by irradiation of  $MgF_2$  crystal at  $T < 50$  K.  $F$ -centers survival efficiency at these temperatures is about 2%.

At  $T > 50$  K sharp reduction of  $F$ -centers accumulation (and survival) efficiency occurs. At the same temperature off-type STE emission quenching,  $H$ -centers delocalization, the growth of on-type STE formation efficiency, the annealing of  $F$ -centers accumulated at low temperatures at  $T = 50-75$  K [6] can be observed. It is evident that all these processes are connected with the oscillation amplitude growth of STE nucleus at  $T > 50$  K and  $H$ -center ( $F_2$ -ion). However, at  $T < 160 - 180$  K, thermal energy is not large enough to completely separate  $F, H$ -pairs (the jump of the  $H$ -center from  $F$ -center) and the main part of them

annihilates (the jump of the  $H$ -center towards  $F$ -center) in correlated pairs.

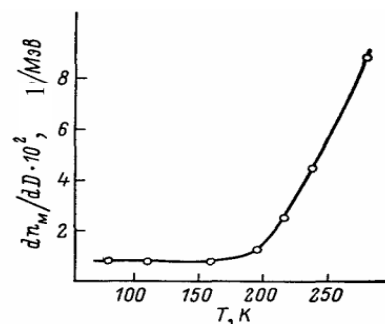


Fig. 4. Temperature dependence of  $MgF_2$   $F_2$ -centers destruction during irradiation by electrons with the energy of 1.2 MeV

These processes completely keep within the accumulation model presented in [7]. On the basis of this model, the processes of color centers accumulation in ionic crystals by mathematic modeling were analyzed [8]. In the model, spatial separation of  $F, H$ -pairs components in ionic crystal consists of two consecutive stages. At the first stage, the function of  $F, H$ -pairs initial distribution at distances between pair components is being formed. The energy sufficient for the separation is transferred to mobile  $H$ -center component from electron excitation decomposing at the place of pair originates and crystal lattice (thermal energy). Further on, separation occurs due to thermal jumps of  $H$ -center (initial distribution function evolution). Considering the researches of  $F$ -center formation processes with femtosecond time resolution, the time of initial distribution function formation is equal to  $\sim 10^{-12}$  s.

The modeling shows that temperature-dependent processes of separation at the stage of initial distribution function formation are of great importance to increase the efficiency of separated  $H$ - and  $F$ -centers formation with the growth of temperature. At low temperatures, initial distribution function is compact, and,  $H$ -centers are in the second or higher coordination spheres in relation to the  $F$ -center only in a small part of pairs. These  $H$ -centers are constant at  $T < 50$  K. As temperature rises, the average distance between Frenkel pair components increases (initial distribution function is more extended). Considering such temperature-dependent process of initial distribution function formation, the calculated temperature dependence of  $F$ -centers accumulation efficiency at different stages determines its type experimentally.

Thus, the pairs, their components being separated at big distances than the closest ones after they have been formed (within around  $10^{-12}$  s), participate in spatial separation and stable centers formation at high temperatures.

### 3.2. Post-Separation Annihilation

We have determined that at 300 K, energy consumption for  $F_2$ -center destruction is equal to the energy spent on  $F$ ,  $H$ -pairs generation (100 eV/center). Thus, at this temperature, the main part of  $F$ -and  $H$ -centers is separated in space. However, at 250 K,  $F$ -centers survival efficiency is very low (0.1 %). The obvious reason is that as the effective generation mechanism during  $H$ -centers traps irradiation in pure  $MgF_2$  crystals lacks, only a small part of them is transformed into stable hole centers and the main part is recombined with  $F$ -centers. This is proved by the high degree of probability of  $H$ -centers interaction with the super-equilibrium  $F_2$ -centers which are their trap. Thus, the difference in color centers accumulation for alkali halide crystals and  $MgF_2$  are completely determined by the difference of  $H$ -center trap generation processes, while temperature dependence of  $H$ -center accumulation efficiency in  $MgF_2$  corresponds to temperature dependence of formation efficiency, these traps are being irradiated by electrons.

It was found out that  $F$ -centers destruction velocity formed during the electron pulse in  $MgF_2$ , is small even at 300 K. For example, at 480 K, the absorption relaxation is represented by the sum of three exponents with  $\tau_1$ ,  $\tau_2$  and  $\tau_3$ , equal to 28.0  $\mu s$ ; 3.0  $\mu s$  and 0.65  $\mu s$ , respectively.  $F$ -centers destruction kinetics does not change if NEB density exceeds by a factor of  $\sim 100$ . Considering the research results of  $F_2$ -centers radiation stimulated destruction, it follows that at high temperature, the components of practically all the formed  $F, H$ -pairs are separated and formed again after  $H$ -centers migration. In other words,  $F$ -centers absorption relaxation kinetics in  $MgF_2$  both at high and low temperatures is limited by recombination processes in close pairs being monomolecular.

### 4. Summary

The process of  $F$ -center accumulation in  $MgF_2$  can be presented as follows. At  $T < 180$  K,  $F$ -and  $H$ -centers separation is the result of athermal  $H$ -center shift. The initial distribution function within this temperature range is formed only due to the energy transferred from electron excitation to  $H$ -center in the place of pair formation, and it consists mainly of close Frenkel pairs. Therefore, the majority of pairs annihilate after

their formation. A small part of  $H$ -centers which are at larger distance from  $F$ -centers, localize at regular lattice sites at  $T < 50$  K (the  $H$ -centers are stable at these temperatures), and insure  $F$ -centers accumulation. At  $T > 50$  K,  $H$ -centers are mobile and cannot be localized in a lattice any more, but the thermal energy is not sufficient enough to remove them from the  $F$ -center. Therefore, most of Frenkel pairs annihilate, the efficiency of  $F$ -centers accumulation in the temperature range from 60 to 180 K is being small. At 180 K, the energy transferred from the lattice to the  $H$ -center becomes much more sufficient than that transferred to the center from electron excitation, and this leads to the growth of Frenkel pair components separation probability in  $MgF_2$  when the temperature increase approaches 1 at  $T > 250$  K.  $F, H$ -pairs separated at longer distances at the stage of initial distribution function formation contribute to  $F$ -centers accumulation. After they have been separated at 250 K, most of  $F, H$ -pairs do not survive, since  $H$ -center trap generation efficiency, i.e. the efficiency of stable hole centers formation in pure  $MgF_2$  crystals is low.  $F$ -centers absorption relaxation kinetics in  $MgF_2$  is limited by the recombination processes in close pairs: correlated pairs, with not separated components at  $T < 180$  K or pairs newly formed after  $F$ -and  $H$ -centers separation and the subsequent diffusion processes at  $T > 180$  K.

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