

The nature and mechanism of formation of radiation-chemical defects in MgO have been studied under steady irradiation [1, 2]. We have investigated radiation-chemical reactions in monocrystalline MgO after microsecond pulses of electrons over a wide range of temperatures.

EXPERIMENTAL

We used two types of MgO single crystals: those with equilibrium vacancy concentrations, obtained by arc melting followed by slow cooling to about 20°C (I); and those with excess concentrations of cation vacancies, created by rapid cooling (quenching) from 1000°C to -196°C (II).

The content of heavy-element impurities in the MgO was determined by atomic adsorption analysis in a Perkin-Elmer 303 apparatus; it was found to be as follows: Fe $1.9 \cdot 10^{-2}\%$; Mn $2.0 \cdot 10^{-3}\%$; Cr $5.8 \cdot 10^{-4}\%$. In (II) crystals, by the ESR method we detected a reduction in the Mn^{2+} concentration in comparison with (I) crystals; on roasting, the Cr^{3+} concentration did not alter appreciably.

Irradiation was effected by means of a U-12 linear electron accelerator (electron energy 5 MeV, pulse current up to 0.2 A, pulse duration 2.3 μ sec). Dosimetry was effected by means of plates of polymethyl methacrylate [3]. The dose per pulse was 3000-10,000 rd. Optical absorption of short-lived particles was registered in a rapid-acting spectrophotometer [4] with an FEU-18A photomultiplier (for 300-590 nm) and an FEU-22 photomultiplier (for 500-1000 nm).

For high-temperature irradiation, the specimens were placed in a furnace with holes for the light and electron beams. A Chromel-Alumel thermocouple was placed adjacent to the specimen. The temperature was continuously measured during the experiment to within $\pm 3^\circ\text{C}$.

Gamma irradiation of the MgO specimens was effected in a GUF-120 apparatus at the Institute of Physical Chemistry of the Academy of Sciences of the USSR (power 120,000 g-eq Ra) at 20 or -196°C. The absorbed dose rate was 2.0-3.4 Mrd/h. The optical absorption spectra of the gamma-irradiated single crystals were recorded in a Hitachi EPS-3T spectrophotometer at 20 or -196°C.

The ESR spectra were recorded in an RE-1301 radiospectrometer (current frequency 9 GHz, modulation frequency 875 kHz). The g factor was measured in comparison with DPPH ($g = 2.0036$). The concentration of paramagnetic centers was determined by comparing the integral intensities of the signals from the specimens with an ultramarine standard.

DISCUSSION OF RESULTS

Figure 1 shows the optical absorption spectra of short-lived particles in (I) and (II), recorded at the end of the electron pulse at 50°C. The spectrum of MgO(I) (curve 1) has a maximum at 350-400 nm with a smooth fall toward longer wavelengths; the spectrum of MgO(II) (curve 2) has a marked maximum at 500-600 nm and a less marked one at 350-410 nm. If (II) is heated to above 500°C, slowly cooled, and again subjected to a pulse of radiation, the maximum at 500-600 nm does not appear (curve 3). Irradiation of a requenched crystal restores curve 2. When repeatedly quenched specimens are irradiated, there is a change in the ratio between the absorption intensities in the regions 350-410 and 500-600 nm, i.e., the intensity at 350-410 nm increases.

To identify the absorption bands we compared the spectra of pulse-irradiated crystals (Fig. 1) with the optical spectra (Fig. 2) and ESR spectra of gamma-irradiated specimens.

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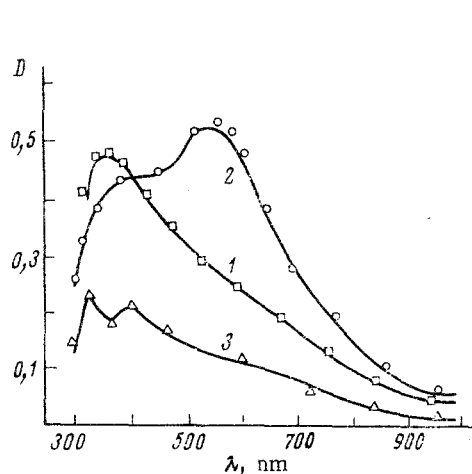


Fig. 1

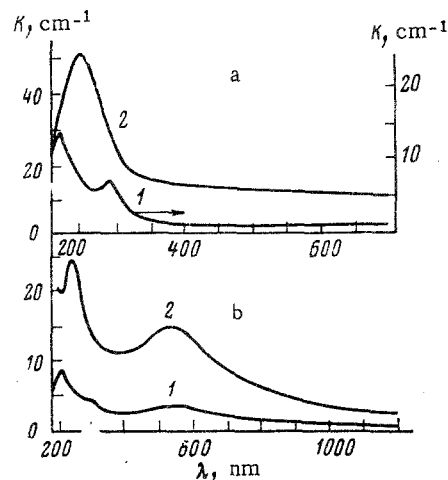


Fig. 2

Fig. 1. Optical absorption spectra of short-lived particles in MgO single crystals irradiated with electron pulses at 50°C, recorded at the end of the pulse. 1) (I); 2) (II); 3) (II) after heating to 500°C, slow cooling to 20°C, and reirradiation. Values of D recorded at 10-nm intervals. Curves plotted from means of 3-5 points.

Fig. 2. Optical absorption spectra of single crystals of (I) (a) and (II) (b), gamma-irradiated at 20°C (1) and -196°C (2). The curves represent the differences between the spectra of gamma-irradiated and untreated single crystals, as recorded on the spectrophotometer.

The absorption bands with maximum at 250 nm and half-width $W_{1/2} = 0.9$ eV in (I) and (II) gamma-irradiated at -196°C correspond in annealing temperatures and accumulation curves to isotropic singlets with $g = 2.002$ in the ESR spectra and can be assigned to F^+ centers [5].

The absorption band with maximum at 540-550 nm formed in the gamma-irradiated specimens of (II) (Fig. 2a) vanishes near 20°C, like the anisotropic singlets with $g_{\perp} = 2.038$ and $g_{\parallel} = 2.002$ in the ESR spectra, and is attributed to V^- centers, following [6, 7]. In the ESR spectra of (I) we also observe anisotropic singlets corresponding to V^- centers, but their concentration is three or four times smaller. The absorption bands at 220 and 290 nm can be attributed to the impurity Fe^{3+} [6].

The oscillator forces for the F^+ and V^- centers were found by means of the equation of Smakula and Dexter [8] for a line of Gaussian shape:

$$N_0 f = 0.87 \cdot 10^{17} \frac{n}{(n^2 + 2)^2} \cdot W_{1/2} \cdot k_{\max}$$

where N_0 is the concentration of centers according to the ESR spectra, f is the oscillator force, n is the refractive index at λ_{\max} ($n_{250} = 1.8450$, $n_{540} = 1.7412$ [9]), $W_{1/2}$ is the half-width of the absorption line in electron-volts, and k_{\max} is the absorption coefficient in cm^{-1} . For an F^+ center, $f = 0.9-1.0$, which is close to the value found for F^+ centers in neutron-irradiated single crystals [10], but different from that found by Chen et al. [11]. For the V^- center, $f = 0.10-0.15$, which is close to the value found by Chen and Sibley [6].

If we analyze the overall optical spectra of pulse-irradiated and gamma-irradiated quenched single crystals of (II) into their Gaussian components, we get practically the same bands, with maxima at 550 nm ($W_{1/2} = 0.48 \pm 0.02$ eV), 400 nm ($W_{1/2} = 0.37 \pm 0.02$ eV), and 330 nm ($W_{1/2} = 0.36 \pm 0.01$ eV). The same bands are seen in the overall short-lived absorption spectrum of (I) recorded at 50°C.

On the basis of these comparisons we can refer the short-lived absorption with maximum

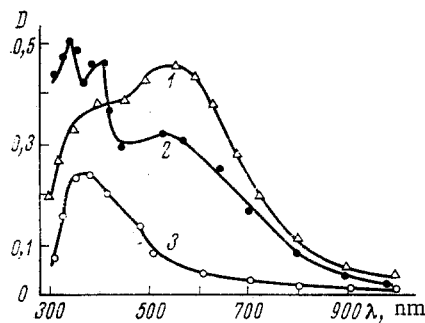


Fig. 3

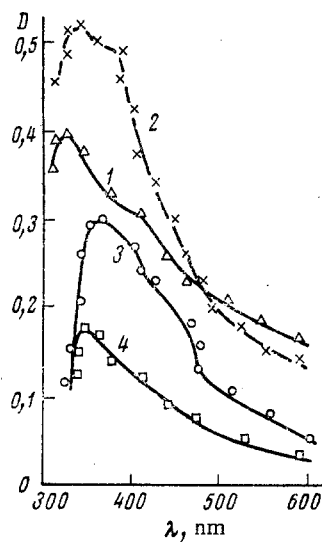


Fig. 4

Fig. 3. Short-lived absorption spectra of (II) recorded at end of electron pulse at 50-500°C: 1) 50°C; 2) 300°C; 3) 500°C.

Fig. 4. Short-lived absorption spectra of (I): 1) at 50°C; 2) 300°C; 3) 500°C; 4) 600°C.

TABLE 1. Radiation-Chemical Yields $G(V^-)$ of V^- Centers in Pulse-Irradiated and Gamma-Irradiated Single Crystals of (I) and (II)

Specimen	$G(V^-)$, particles/100 eV		
	gamma-irradiation		pulse irradiation
	20°	-196°	50°
(I)	0,05 *	0,2 *	1,7
(II)	0,2	0,8	3,2

*According to ESR spectra.

at 550 nm to a V^- center. The attribution of the absorption bands with maxima at 350 and 400 nm is still difficult. In the ESR spectra, when (I) or (II) is irradiated the sextet of Mn^{2+} becomes more intense than that of a nonirradiated specimen. However, the optical spectra of gamma-irradiated and pulse-irradiated (I) and (II) cannot be attributed to absorption of the impurity Mn^{2+} in an octahedral environment. It is more likely that the absorption bands at 350 and 400 nm are due to absorption by Mn^{3+} or Mn^{4+} ions.

Thus, resolution of the optical spectra of gamma-irradiated and pulse-irradiated single crystals of (I) and (II) into their Gaussian bands leads us to the conclusion that the same particles are formed by steady and pulsed irradiation, but in different concentrations.

From Table 1 we see that the radiation-chemical yields of V^- centers, calculated from the optical spectra by the method in [8], are 15-20 times greater in the pulse-irradiated crystals than in the gamma-irradiated crystals at 20°C, and 4-8 times greater than in the gamma-irradiated crystals at -196°C.

In pulse-irradiated (I) and (II) at 20°C, the lifetimes of the particles due to absorption at 350-400 and 500-600 nm are similar, and the half-decay period $\tau_{1/2}$ is $1 \cdot 10^{-2}$ for both regions. The centers are not destroyed by the action of light, because a tenfold change

TABLE 2. Half-Lives and Destruction Rate Constants (sec^{-1}) of Centers in Pulse-Irradiated (I) and (II)*

T., °C	(I)		(II)	
	300—400 nm	500—600 nm	300—400 nm	500—600 nm
50	$\tau_{1/2}=0,6 \cdot 10^{-2} \text{sec}$	$\tau_{1/2}=1,0 \cdot 10^{-2} \text{sec}$	$\tau_{1/2}=0,7 \cdot 10^{-2} \text{sec}$	$\tau_{1/2}=1,0 \cdot 10^{-2} \text{sec}$
200	$\tau_{1/2}=0,6 \cdot 10^{-2} \text{sec}$	$1,0 \cdot 10^3$	$\tau_{1/2}=0,4 \cdot 10^{-2} \text{sec}$	$\frac{0,7 \cdot 10^3}{0,3 \cdot 10^3}$
300	$\frac{2,5 \cdot 10^2}{0,2 \cdot 10^2}$	$\frac{3,6 \cdot 10^3}{2,5 \cdot 10^2}$	$\frac{2,3 \cdot 10^2}{0,4 \cdot 10^2}$	$\frac{5,3 \cdot 10^3}{5,8 \cdot 10^2}$
400	$\frac{5,0 \cdot 10^3}{1,8 \cdot 10^3}$	$\frac{3,5 \cdot 10^4}{0,5 \cdot 10^4}$	$\frac{4,8 \cdot 10^3}{2,0 \cdot 10^3}$	$\frac{1,5 \cdot 10^4}{2,9 \cdot 10^3}$
500	$\frac{2,8 \cdot 10^4}{0,9 \cdot 10^4}$	$\frac{4,6 \cdot 10^4}{2,6 \cdot 10^3}$	$\frac{5,7 \cdot 10^4}{1,2 \cdot 10^4}$	$\frac{5,4 \cdot 10^4}{0,4 \cdot 10^4}$
600	$\frac{3,0 \cdot 10^4}{1,0 \cdot 10^4}$	—	$\frac{5,0 \cdot 10^4}{1,2 \cdot 10^4}$	—

*The figures above the line are the values of k_1 (up to $\sim 500 \mu\text{sec}$), those below the line are the values of k_2 .

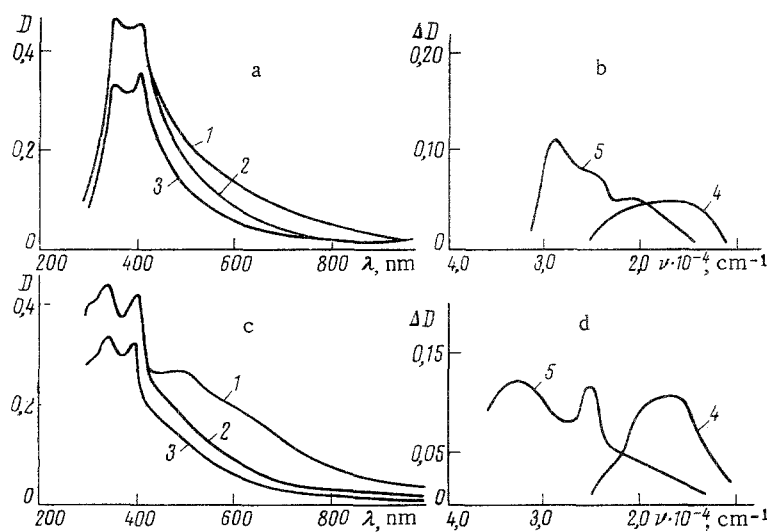


Fig. 5. Short-lived absorption spectra at 300°C; a) (I); b) (II). 1) Spectra at end of electron pulse; 2) 50 μsec after end of pulse; 3) 450 μsec after end of pulse. b, c) Differential spectra constructed from differences between spectra 1 and 2 (curve 4) and between spectra 2 and 3 (curve 5).

in the intensity of the light beam does not appreciably affect the rate of destruction, while a filter which cuts off the short-wave part of the spectrum does not affect the optical density at the end of the pulse. However, the V^- centers obtained by gamma irradiation are unstable under the influence of light, in agreement with [1].

From Fig. 3 we see that when the irradiation temperature is raised, the concentration of V^- centers (absorption region 500–600 nm) decreases, while the optical density in the region 300–400 nm at 300°C increases but then begins to decrease; but at 500°C, centers absorbing in this region are formed. A similar change is observed for (I) in the character of the spectrum as the irradiation temperature is raised (Fig. 4).

Between 50 and 250°C for the absorption region 300–400 nm there is an increase in optical density after the end of the pulse. This suggests that the centers responsible for absorption at 300–400 nm are not formed by the direct action of the radiation but as a result of secondary processes, e.g., by interaction with a slowly diffusing electron. This pattern is characteristic of impurity ions [12], and undoubtedly supports our hypothesis that the absorption at 300–400 nm is due to ions of the impurity manganese. Over the whole temperature

range, in the region 500-600 nm the optical density decreases with the elapsed time after the pulse.

From Fig. 5 we see that the centers which absorb at 400-1000 nm are destroyed in the first 50 μ sec (b and d, curves 4). Analysis of these differential spectra into Gaussian bands reveals that the main component of the spectrum is the band with $\lambda_{\text{max}} = 620$ nm, $W_{1/2} = 0.4$ eV, while the band at 540 nm is very small. The appearance of bands at 620 nm at 300°C can be attributed either to the appearance of Cr^{3+} and Fe^{2+} or to aggregation of V^- centers characteristic of MgO [13]. In the spectra at 50-450 μ sec (Fig. 5, b and c, curves 5) we can discern bands with maxima at 540, 500, and 300-330 nm, corresponding to absorption by a V^- center and an Mn impurity ion.

On considering the kinetics of destruction of the short-lived absorption in pulse-irradiated MgO single crystals, we can discern two absorption regions, 300-400 and 500-600 nm. The time dependences of destruction of the color centers (at 300°C or higher) have at least two regions, each of which gives a straight line when $\log C$ is plotted vs t .

From Table 2 we see that for (I) and (II) the corresponding absorption regions have similar destruction rate constants at all the temperatures studied. If we compare the 300-400 and 500-600 nm regions, we find that at 50°C the values of $\tau_{1/2}$ for the color centers are nearly the same, but at high temperatures the rate constants for destruction of the centers which absorb at 500-600 nm are higher than those for 300-400 nm. At 200-500°C, the effective activation energy of destruction of the V^- centers is 11.5 kcal/mole for the centers absorbing at 300-400 nm; at 300-600°C the figures are 21-24 kcal/mole. Consequently, these centers disappear independently. The first-order reaction of destruction of the V^- center can be attributed to emergence of a hole into the conduction band followed by capture by structural defects.

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CONCLUSIONS

1. In the short-lived absorption spectra of pulse-irradiated MgO single crystals the authors have identified absorption bands belonging to V^- centers and manganese impurity ions.

2. The radiation-chemical yields of V^- centers in pulse-irradiated specimens are higher than those in gamma-irradiated ones.

3. The authors have studied the kinetics of destruction of color centers in pulse-irradiated MgO single crystals. They have calculated the rate constants and effective activation energies.

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