Photoconversion of F^+ centers in neutron-irradiated MgO

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Abstract

In neutron-irradiated MgO crystals, experiments and theory demonstrate that photon excitation of the positively charged anion vacancies (F^+ centers) at 5.0 eV releases holes that are subsequently trapped at V-type centers, which are cation vacancies charge-compensated by impurities, such as Al^{3+}, F^-, and OH^- ions. A photoconversion mechanism occurs very likely via electron transfer to F^+ centers from the *quasi-local states* which are induced in the valence band. INDO quantum chemical simulations of F^+ centers confirmed the appearance of two induced quasi-local states located at 1.2 and 2.0 eV below the top of the valence band. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

It was long ago observed [1,2] that optical excitation of F^+ centers (an oxygen vacancy that has trapped an electron) in corundum (α-Al_2O_3) results in the formation of two-electron F centers. This process of color photoconversion is accompanied by the formation of hole centers [1–3]. The latter precludes a simple explanation which assumes thermal ionization of an excited F^+ center with the electron further trapped by another F^+. On the basis of semi-empirical INDO calculations of F-type centers, the creation of hole centers under photoexcitation was suggested [4]. It was stressed that the proposed model is quite general for ionic solids where charged point defects strongly disturb surrounding ions. In particular, it holds for Tl^{2+} centers in alkali halides and LiF:Mg [5].

The present communication addresses photoconversion of the two charge states of the anion vacancies in neutron-irradiated MgO: F^+ and F centers. In MgO, both the F^+ and F centers absorb at nearly the same energy, 4.92 and 5.01 eV, respectively [6]. In neutron-irradiated MgO, the predominant charge state of the anion vacancy is the F^+ center, i.e., anion vacancies are primarily in the one-electron state [7]. Therefore in the present

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study we will address only $F^+ \rightarrow F$ photoconversion. In Section 2, we present results of theoretical simulations of the F^+ and F centers and their photoconversion. In Section 3, experiments are presented complementing theory, in particular, hole release as a product of this process. The main results are summarized in Section 4.

2. Theory

In this study we have used the semi-empirical method of the intermediate neglect of the differential overlap (INDO), which is a simplified version of the Hartree–Fock formalism. Its modification is described in [8,9]. INDO allows simulations of quantum clusters containing hundreds of atoms with optimization of lattice geometry around defects. Additional details regarding its application to MgO crystals can be found in [10–12]. Good agreement with a number of experimental data was achieved and several experiments (on the luminescence of the F centers and their diffusion) interpreted. Important for this paper is that the positions of the ground state levels for both F^+ and F centers are predicted to be 3 eV above the top of the valence band, and their excited states lie very close to the bottom of the conduction band. This suggests a trivial explanation for the photostimulated F-type center transformation – an electron of the excited F^+ center could be ionized into the conduction band and then trapped by another F^+ center, thus giving rise to the two-electron F center. In this case, no new defects are expected to arise except bare O vacancies.

In this work, we have used the same 125-atom clusters of a cubic shape having O_h symmetry and embedded into the electrostatic field of the rest of the crystal. Analysis of the F^+ results shows the presence of two quasi-local states induced by a charged defect in the valence band (VB) (see Fig. 1(a)). These levels are located at 1.2 and 2.0 eV below the top of the VB. Their molecular orbitals consist mainly of atomic orbitals of O atoms of the two spheres surrounding the O vacancy, at $(1,1,0)$ and $(2,0,0)$ in the Mg–O lattice spacing units (Table 1). Since the ground state energy level of the
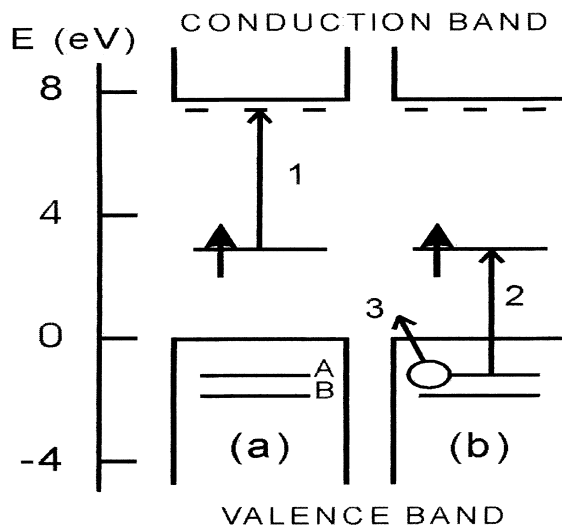

Fig. 1. Schematic model of the photoconversion mechanism. (a) Traditional model via F^+ center electronic excitation (1) and electron release to the conduction band. (b) A novel mechanism based on the electron transition to the ground state of the F^+ center (2) from the quasi-local states induced by a charged defect which leads to hole formation in the VB (3).

Table 1
Coefficients of atomic orbitals in the molecular orbital in the two quasi-local energy states (A and B in Fig. 1(a)) induced in the valence band by the F^+ center (coordinates are in units of the Mg–O distance in the perfect lattice)

Atom	Level A	Level B
O $(1,1,0)$	$p_x = -0.204$	$p_x = -0.041$
	$p_y = 0.204$	$p_y = -0.041$
	$p_z = -0.1374$	$p_z = 0.0$
O $(2,0,0)$	$p_x = 0.04$	$p_x = 0.307$
	$p_y = -0.035$	$p_y = 0.0$
	$p_z = 0.0$	$p_z = 0.0$

F^+ center lies 3 eV above the VB top, the excitation energy of the electron from the quasi-local state is close to that for the F^+ center electronic excitation (5 eV). Based on this observation, we suggest the following novel interpretation of the F-type center photoconversion: under excitation with 5 eV photons, some of the F^+ centers do not become electronically excited into the 2p-type state, rather, electrons are photoexcited from the quasi-local states in the VB (Fig. 1(b)) to the ground

state of the F^+ centers; as a result F centers in the ground state are produced. Simultaneously, *holes* are produced on the quasi-local levels. Since it is degenerate in energy with the VB, a hole is released into the latter and moves within the crystal until it is trapped by some impurity or defect. Creation of hole centers under photostimulation is a key feature of our photoconversion model

$$F^+ + hv \; (5.0 \; \text{eV}) \rightarrow F + h^+, \tag{1}$$
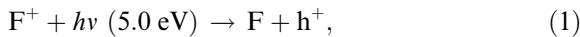
where h^+ is a hole in the valence band which eventually becomes a hole center. This prediction was tested in the experiments discussed below.

3. Experimental

The MgO crystal used was grown at the Oak Ridge National Laboratory using the arc fusion technique [13]. The starting material was MgO powder from the Kanto Chemical, Japan. Neutron irradiation was carried out in the Oak Ridge Bulk Shielding Reactor to a dose of 5.3×10^{15} neutrons/cm^2 ($E \geqslant 1$ MeV). The irradiating temperature was estimated to be 320 K. A Perkin-Elmer, Lambda 19 spectrophotometer was used in the uv-vis-ir region. Far-infrared data were taken with a Perkin-Elmer FT-IR 2000 spectrophotometer. The sample was excited with a low-intensity 5.0 eV light, the source being a 400 W Xe lamp in conjunction with a 7200 Oriel monochromator set at 250 nm.

The neutron-irradiated crystal was excited with 5.0 eV light. These photons in principle will excite both F^+ and F centers, since they both absorb light at nearly the same energy. Given that in neutron-irradiated crystals the anion vacancies are primarily in the paramagnetic F^+ charge state, any photoconversion will primarily involve the release of a hole from an F^+ center according to Eq. (1).

Optical absorption measurements were used to determine where the holes are ultimately trapped. The result of the excitation with 5.0 eV light is shown in Fig. 2. With continued excitation, an absorption band centered at 2.3 eV increased. The absorption coefficient at 5.0 was essentially unchanged, because the resulting F band still ab-
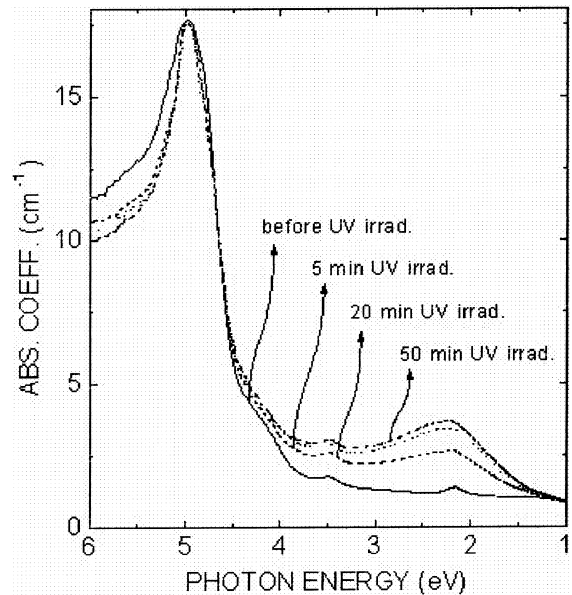

Fig. 2. Optical-absorption spectra of a neutron-irradiated MgO crystal before and after UV irradiations (crystal thickness: 3.1 mm).

sorbed at 5.0 eV. The 2.3 eV band is known to be due to holes trapped at centers compensated by Al^{3+}, F^- or OH^- ions [14].

The resulting defects, referred to as V_{Al}, V_F or V_{OH} centers, are due to

$$V_{Al}^- + h^+ \rightarrow V_{Al}, \tag{2}$$

$$V_F^- + h^+ \rightarrow V_F, \tag{3}$$

$$V_{OH}^- + h^+ \rightarrow V_{OH}, \tag{4}$$

where the linear configurations are Al^{3+}–O^{2-}–[Mg vacancy]–O^-; Mg^{2+}–F^-–[Mg vacancy]–O^-; and Mg^{2+}–OH^-–[Mg vacancy]–O^-, respectively [14]. The O^- represents an O^{2-} ion with a trapped hole. The trapped holes at these centers are metastable and have a half-life of several hours at room temperature. We also note that during excitation, the charge transfer band of Fe^{3+} at 4.3 eV also increased [15]. The differential spectrum shown in Fig. 3 shows that the Fe^{3+} band emerged along
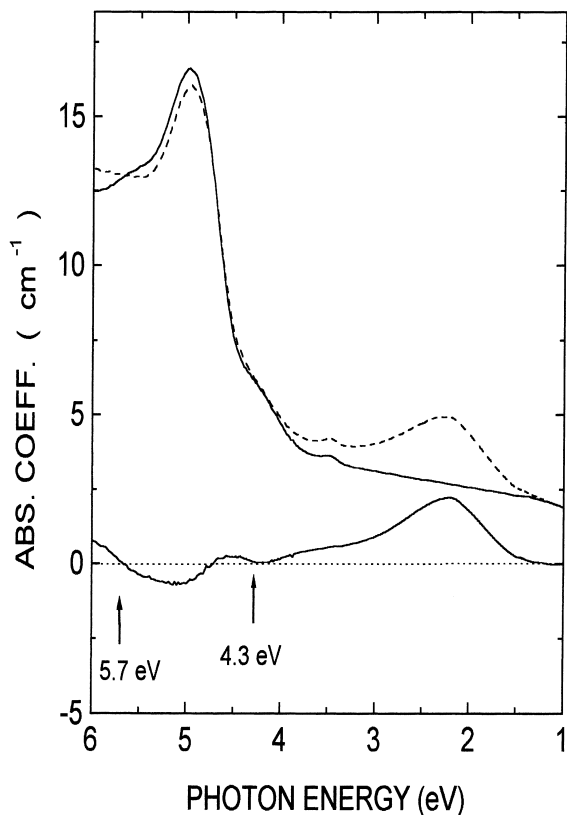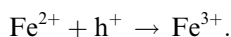
Fig. 3. Differential spectrum of the *n*-irradiated MgO crystals before and after UV irradiation for 50 min. The spectrum was obtained with respect to the initial spectrum.
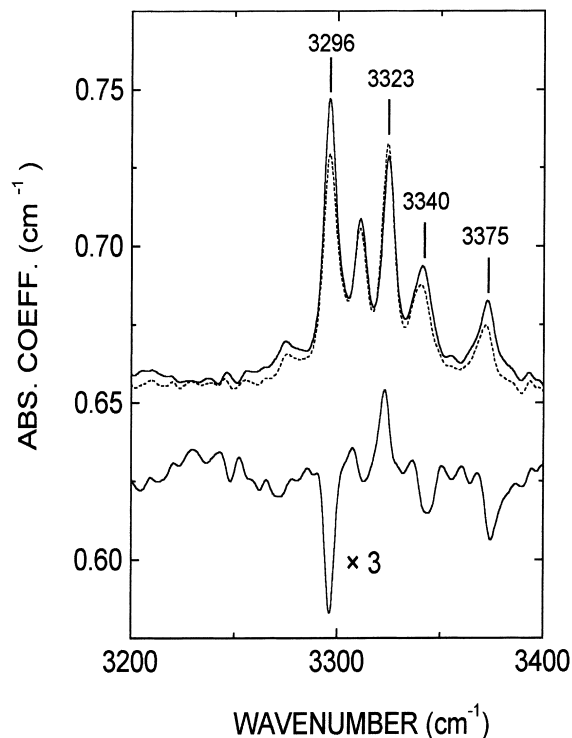

Fig. 4. Top infrared optical-absorption spectra of an *n*-irradiated MgO crystal before (solid line) and after UV irradiation for 1 h (dotted line). The differential spectrum (bottom) is enlarged by a factor of 3.

with the 2.3 eV band. This indicates that the released holes are also trapped at Fe^{2+} sites, resulting in the following reaction:

$$Fe^{2+} + h^+ \rightarrow Fe^{3+}.$$

Infrared spectroscopy was used to demonstrate that holes are trapped at the V_{OH}^- to form the V_{OH} centers. It is known [16,17] that the OH^- stretching frequency of the V_{OH}^- center occurs at 3296 cm^{-1} and that for the V_{OH} center it is at 3323 cm^{-1}. The infrared spectra before and after excitation with 5.0 eV light are shown in Fig. 4. The differential spectrum is shown at the bottom. It is clear that during excitation V_{OH} centers are formed at the expense of V_{OH}^- centers, indicating that holes have been trapped.

4. Summary

The combination of theory and experiment presented in this paper strongly supports the F-type center photoconversion mechanism via electron transfer to the F^+ center from the quasi-local states induced in the valence band. Thus, F centers and holes are produced; the latter are subsequently trapped at impurities (primarily Fe^{2+} ions and cation vacancies charge-compensated by impurities, such as Al^{3+}, F^- and OH^- ions).

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