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Nature of the 6.1-eV band in neutron-irradiated Al_2O_3 single crystals*

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The optical absorption band in single-crystal Al_2O_3 at 6.1 eV associated with atomic-displacement-type damage has been investigated through its relationship with the 3.0-eV V_{OH}^- hole center whose identity had been previously established. Using lightly-neutron-irradiated [(1–4) × 10^{15} reactor neutrons/cm^2] thick crystals to facilitate measurement of the absorption spectra, it was shown that subsequent room-temperature ^{137}Cs γ irradiation produced a further enhancement in the 6.1-eV band as well as developing a composite V band near 3.0 eV whose intensity bears a linear relationship to that of the 6.1-eV band. Optical bleaching at 410 nm (3 eV) decreases both the V and 6.1-eV bands again with a linear relationship which indicates an oscillator-strength ratio of f_{204}/f_{410} of ~ 19. Irradiation in the 6.1-eV band likewise causes a decrease in the 410-nm region. These results indicate that (i) the 6.1-eV nm band is due to an electron trapped at some defect termed the *d* center produced by atomic-displacement processes, and (ii) the 6.1-eV band reflects the concentration of trapped holes rather than the concentration of *d* centers. Isochronal annealing causes thermal decay of the 6.1-eV band in the range 300 to 600° C in these reactor-irradiated specimens.

I. INTRODUCTION

The most prominent feature of the optical absorption spectrum of neutron-irradiated single-crystal Al_2O_3 (corundum) is an absorption band at 204 nm (6.1 eV). This band was first observed by Levy and Dienes[1] and subsequently studied by a number of investigators.[2–4] Electron-bombardment experiments by Arnold and Compton[5] demonstrated that particle bombardment sufficiently energetic to displace lattice ions is necessary to produce the defects responsible for the 6.1-eV band. Recently Arnold *et al.*[6,7] have explored the production of this absorption band by ion-implantation using H^+, D^+, $^3He^+$, $^4He^+$, N^+, O^+, Ar^+, and Ar^{++} in the energy range from 40 to 500 keV. They found that in addition to requiring lattice displacements, the yield of defects responsible for the 6.1-eV band (henceforth termed *d* centers) is also sensitive to the intensity of ionization during or subsequent to irradiation.

The origin of the 6.1-eV band is uncertain. In their study of the threshold energy for the production of this band by electron bombardment, Compton and Arnold[8] concluded that the displacement energy was 40 eV if Al^{3+} were the displaced ion and 70 eV if O^{2-} were involved. Because of this, several investigators have concluded that the 6.1-eV band is associated with an Al^{3+} defect, i.e., an Al^{3+} vacancy or an Al^{3+} interstitial, which has captured one or more holes or one or more electrons, respectively. However, Levy[3] has pointed out that the yield of *d* centers is small and the band gap of Al_2O_3 is ~ 9 eV. Therefore, there is much room in the unexplored vacuum uv for additional absorption bands which might be associated with primary defects. Therefore, he cautioned that the 6.1-eV band could be associated with some simple type of defect cluster. Multiple vacancies might be responsible or even a complex like the one whose ESR has been investigated by Gamble *et al.*[9]

In this paper we will use information gained about a specific hole band, namely, the V_{OH}^- band, to draw inferences about the nature of the 6.1-eV band in reactor-irradiated Al_2O_3. Our recent study[10] of thick Al_2O_3 single crystals before and after γ irradiation has revealed that a pair of ir OH^- stretching bands at 3278 and 3316 cm^{-1} behave analogously to corresponding bands in MgO which are associated with OH^- ions adjacent to cation vacancies before and after hole trapping. The OH^- stretching mode that grows during γ irradiation at the expense of the stretching mode present before irradiation scales upon both irradiation and bleaching with the intensity of a previously observed[11] band near 410 nm (3.0 eV). This band is analogous to the composite V band at 2.3 eV in MgO.[10,12] Therefore, this behavior suggests that the 3.0-eV band is due to trapped holes and that an important component of this band is the V_{OH}^- center absorption. It was further established that optical bleaching in the 3-eV band destroyed a band at 5.46 eV identified with a transition involving the Cr^{2+} ion, present as an impurity in the crystals. Thermal annealing produced a similar correlated decay of the two bands and the spectrum of the 170 °C thermoluminescent glow peak associated with this thermal decay corresponds to the R line of ruby at this temperature. Evidently the thermal decay occurs by a release of a hole from the V_{OH}^- band and its recombination with an electron on the Cr^{2+} which results in the emission of the excited Cr^{3+}. All of these points of evidence indicate that the absorption near 3.0 eV is indeed associated with V-type trapped hole centers. Using this information it should be possible to use the behavior of this band relative to the 6.1-eV band to learn something about the latter.

II. EXPERIMENTAL PROCEDURE

Samples used in this work were uv-grade Linde sapphire grown by the Czochralski technique. Rod-shaped specimens approximately 4 cm in length were used. This length was necessary to detect with reasonable precision the ir absorption associated with the ~ 10^{15} OH^- ions/cm^3 introduced into the crystals during growth. The axes of the specimens were inclined 60° to the *c* axis. Reactor-spectrum neutron irradiation was performed in the North Carolina State University Pulstar reactor which has a flux of 10^{13} neutrons/cm^2 sec. Although the samples were irradiated in ice (~ 0 °C) it was necessary to keep them in a holding tank at 40 °C for the decay of radioactivity for six days following reactor exposure. All γ irradiations were performed at ~ 35 °C in a ^{137}Cs γ-ray source whose intensity is ~ 10^6 R/h. Optical absorption measurements in the visible and near uv were carried out using a Cary 14R spectrophotometer with a matched unirradiated crystal in the reference path. Spectral data were analyzed and plotted using a Digital PDP-12 data acquisition system which employs a Calcomp plotter. Infrared measurements of the OH^- stretching modes were made in a Perkin Elmer 467 ir spectrophotometer. Isochronal annealing of irradiated crystals was accomplished in a muffle furnace preset to the desired temperature and 10 min annealing periods were used at each temperature. The large specimen mass with its appreciable thermal inertia significantly affected the rise time and quench rate producing a slight change in effective pulse length as the temperature increases.

Optical bleaching was achieved with a 150-W mercury-xenon source which was dispersed by a Bausch and Lomb high-intensity monochromator.

III. RESULTS AND DISCUSSION

In order to compare the optical and thermal bleaching characteristics of the 6.1-eV band with those of the composite *V* band, it is necessary that the concentration of absorption centers for the two be comparable. The density of V_{OH}^- native hole trapping centers is quite small (~ 10^{15} cm^{-3}). Therefore, care had to be taken to restrict the fast-neutron dose to small values so that the neutron damage would not swamp out the effect of the characterized hole traps. For this reason integrated neutron exposures were usually kept in the range $(1-4)\times10^{15}$ neutrons/cm^2.

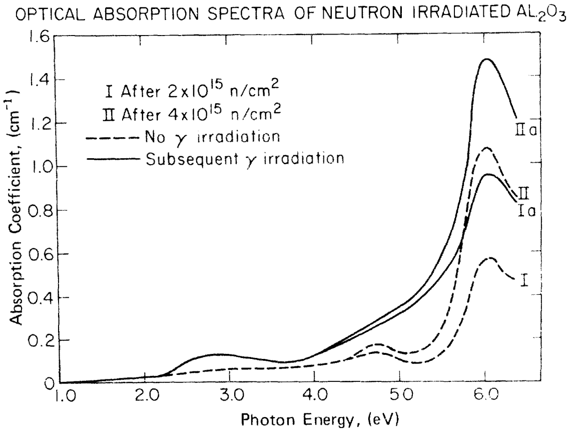

FIG. 1. Absorption spectra of neutron-irradiated uv-grade Al_2O_3 measured at room temperature. The dashed curves were measured approximately one week after reactor exposure; the solid curves after a subsequent 5-min γ irradiation in a source intensity of ~ 10^6 R/hr.

The dashed curves in Fig. 1 show the absorption spectra for two 3.7-cm-long Al_2O_3 crystals from the same batch after exposure of 2×10^{15} and 4×10^{15} neutrons/cm^2. Upon γ irradiation (5 min at ~ 10^6 R/h) the 6.1-eV band was much enhanced and the composite *V* band developed (solid curves). It is significant that the native hole centers do not come appreciably into play until the subsequent γ irradiation. This point will be considered below. In a series of γ-ray exposures of 20–40 sec each it was found that after the first exposure there is a linear relation between the increment of the 6.1-eV band and the intensity of the 3.0-eV band. The growth of the *V*-band intensity toward saturation during γ irradiation is the same for the two specimens differing a factor of 2 in neutron exposure and it is significant that the amount of the 6.1-eV-band enhancement is also the same in each case. The increase in absorption coefficient $\Delta\alpha_{204}$ is 0.45 cm^{-1} at saturation as can be seen from Fig. 1. A third crystal from the same set (not shown in Fig. 1) which was exposured to only 1×10^{15} neutrons/cm^2 showed the same saturation $\Delta\alpha_{204}$ upon γ irradiation and virtually the same composite *V*-band development.

These observations indicate two things: (a) the 6.1-eV-band enhancement is due to the availability of electrons resulting from native *V*-type hole trapping centers already present. (b) The neutron-produced *d* centers responsible for the 6.1-eV band are not all in the proper charge state to contribute to this band after neutron bombardment. The ionization accompanying γ irradiation is able to fill hole traps and convert more *d* centers into 6.1 eV absorbers at the same time. This is strong evidence that the *d* centers are electron traps and the center responsible for 6.1 eV absorption is a *d* center which has captured an electron. Since such a short γ-ray exposure is required to saturate the 3.0-eV band, it is surprising that the reactor irradiation itself did not develop this band

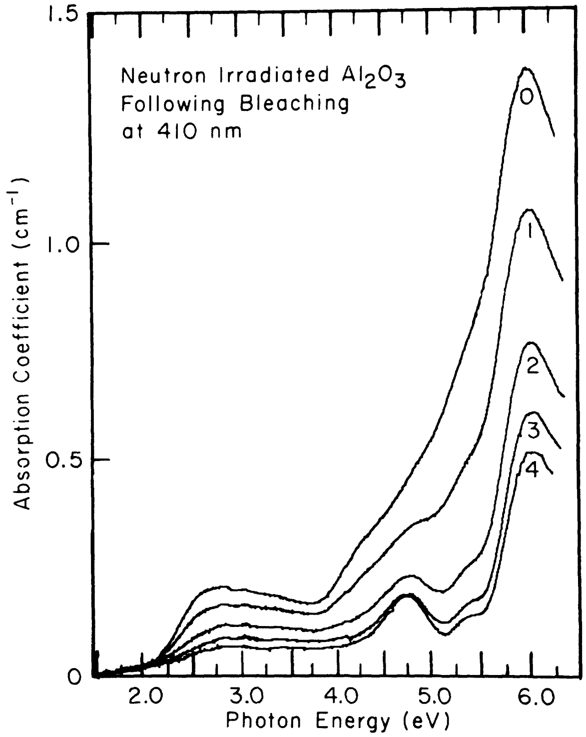

FIG. 2. Effect of optical bleaching with 410-nm light on the absorption spectra of Al_2O_3 after neutron irradiation (4×10^{15} neutrons/cm^2) and γ irradiation. Bleaching times are: curve 0—0 min, curve 1—5 min, curve 2—15 min, curve 3—35 min, curve 4—75 min.

to the full extent. One possible cause for failure to observe this band and the 6.1 eV enhancement that goes with it is connected to the thermal instability of the V_{OH}^- center which has been shown[10] to lose its hole upon heating to ~160 °C. The six days it was stored to 40 °C after removal from the reactor would afford an opportunity for such a decay. A rough estimate of the kinetic parameters required for such a decay to occur indicates that the process is indeed reasonable.

Figure 2 shows the effect of optical bleaching at 410 nm. The curves 0 through 4 result from bleaching times of 0, 5, 15, 35, and 75 min, respectively, for the Al_2O_3 crystal which had received a neutron dose of 2×10^{15} neutrons/cm^2. Again it is clear that there is a direct correlation between the V band and 6.1-eV bands. Figure 3 is a plot of α_{410} vs α_{204} for 2×10^{15} and 4×10^{15} neutrons/cm^2 (curve II). Both curves exhibit a linear slope of 7.6. The drop of curve I at low α values is evidently due to the competition of Cr^{2+} and possibly other electron trapping centers for the holes released by 410-nm light. It is possible to resolve a small Cr^{2+} band at 5.5 eV after the γ irradiation.

From the slopes of curves I and II of Fig. 3 using the half-width of the 6.1-eV band of 0.6 eV due to Levy,[3] the measured half-width of the composite V band of approximately 1.5 eV and Smakula's equation, we find the ratio of oscillator strengths to be $f_{204}/f_{410}\simeq 19$. A similar estimate from previous experiments[10] on γ-irradiated Al_2O_3 yields the ratio $f_{Cr^{2+}}/f_{410}\simeq 2$. Therefore, the oscillator strength of the 6.1-eV band appears to be an order of magnitude larger than that for the Cr^{2+} transition. If it is assumed that the composite V-band oscillator strength is comparable to that of the analogous center in MgO which is reported[13] to be between 0.05 and 0.10, the oscillator strength of the 6.1-eV band would lie in the range 1–2 consistent with values expected for a one- or two-electron center.

It is evident from Fig. 2 that more is occurring during excitation by 410-nm light than correlated bleaching of the bands at 6.1 and 3.0 eV. By taking differences between the before and after bleaching curves, a band at 4.3 eV which undergoes bleaching is clearly resolved as can be seen from Fig. 4. Also detectable in the curves of Fig. 4 is the Cr^{2+} band at 5.5 eV which appears as a shoulder on the 6.1-eV band. Because of the possibility of excitation in the tail of the 4.3-eV band during 410-nm bleaching, it cannot be said from this observation alone whether the 4.3-eV-band bleaching is due to optical excitation or hole capture. Finally, the difference curves of Fig. 4 indicate something about the nature of the 4.8-eV band: Since it is not seen in the difference curves it obviously is not affected by the bleaching process and, therefore, is not destroyed by hole trapping. Tippins[14] has observed a Fe^{3+} charge-transfer transition at this energy but our experiments suggests that such is not its origin here because of

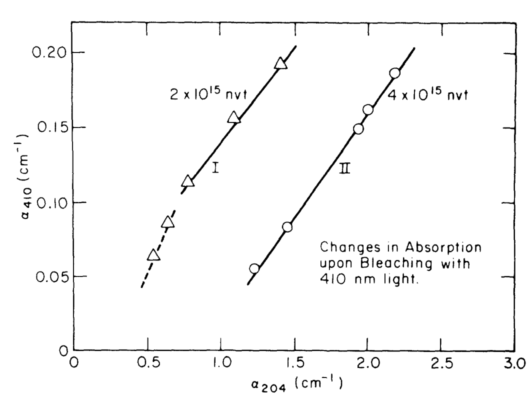

FIG. 3. Variation of absorption in the 3-eV band (α_{410}) compared to that in the 6.1-eV band (α_{210}) with 410-nm bleaching for two neutron-irradiated crystals which received a γ irradiation sufficient to saturate the 3-eV band.

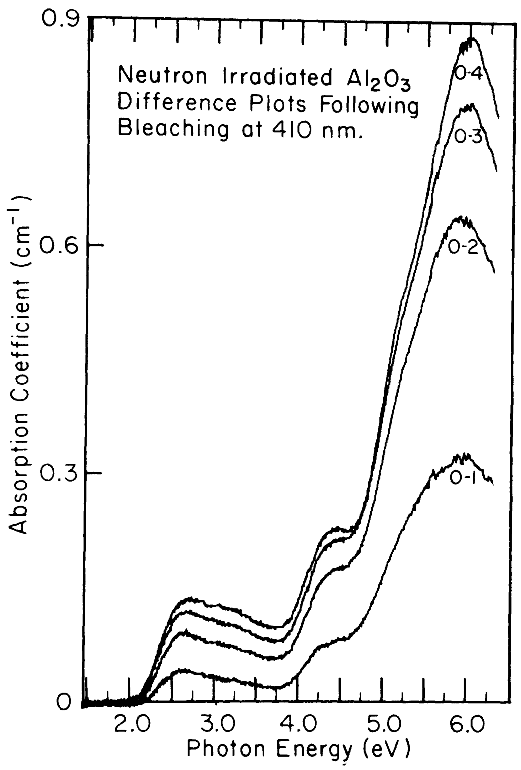

FIG. 4. Change in total absorption as a function of photon energy which results from 410-nm bleaching. Each curve results from substracting a curve of Fig. 2 from the unbleached spectrum; e.g., 0 – 1 represents the difference induced by the first bleach (5 min), etc.

both its insensitivity to bleaching and the fact that it is not present before neutron bombardment which should be the case were Fe^{3+} responsible.

The shape of the band or bands undergoing bleaching in the V region is also clearly delineated in Fig. 4. Here it is noteworthy that, although such a band shape might be accounted for by two or more overlapping Gaussian bands, it is strikingly similar to the shape of the F^- (F') band in the alkali halides for which the optical transition is from a bound state to a continuum of levels. It would be interesting to measure the low-temperature photoconductivity in this region and determine whether the transition in question, presumably of the V_{OH}^-, is indeed a carrier-freeing transition.

A bleaching experiment using 200-nm light was also carried out. The results were not so clear cut as in the case of 410-nm bleaching perhaps because of interference with Cr^{3+} absorption. Nevertheless, a decrease in both the 6.1- and 3.0-eV bands was observed which is additional confirmation of the intimate relation between the two.

Isothermal annealing studies of the thermal decay of both the composite V band and the 6.1-eV band were carried out using 10-min pulses at 50 °C intervals up to 600 °C. The amplitude of these bands was measured after each pulse anneal and again after a subsequent saturating doses of γ rays. This procedure permits thermal emptying of the center or annihilation by recombination with a carrier released from some other trap ("electronic" annealing) to be distinguished from thermal destruction of the center ("ionic" annealing), since the subsequent γ irradiation repopulates those centers which remain. Figure 5(a) records the decay of the composite V band in terms of the relative absorption coefficient α/α_0 vs anneal temperature for a neutron exposure of 4×10^{15} neutrons/cm^2. Curve I is the result immediately after anneal and curve II after the subsequent saturating γ irradiation. From a comparison of curves I and II it is evident that holes are released from these V-type centers in two stages, one between 150 and 200 °C and one between 300 and 350 °C. The first stage corresponds to the 170 °C decay attributed earlier to thermal bleaching of the V_{OH}^- center.[10] Thermoluminescence associated with this stage was observed on another crystal which received a similar neutron dose. As in the case of γ irradiation only,[10] a glow peak near 170 °C was observed; however, the spectral composition was different for the two situations. The γ-irradiated crystal exhibited a glow peak entirely composed of the R

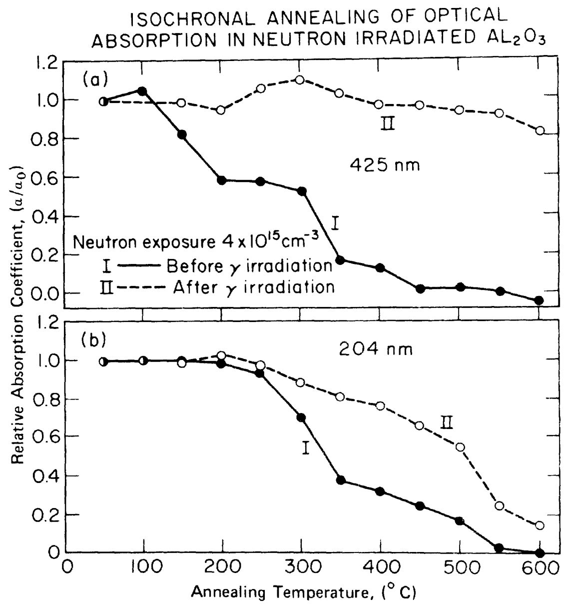

FIG. 5. Isochronal annealing of the intensity (relative absorption) of the composite V-band measured at (a) 425 nm and (b) the 6.1-eV band. The anneal pulses were 10 min at the indicated temperature and the absorption was measured at room temperature.

line of ruby due to Cr^{3+} excitation by the electron-hole recombination, whereas in the present case there is evident in addition to the *R* line a broad emission centered near 3 eV which is evidently associated with recombination at *d* centers or some other defect created by neutron irradiation.

The second annealing stage is apparently due to thermal release of holes from another *V*-type center. It is interesting to note that the *V*-band maximum shifts to ~2.8 eV after the V_{OH}^- decay at 170 °C, emphasizing the composite nature of absorption in this region. Previous isochronal annealing studies of specimens exposed only to γ rays also gave indications of a similar high-temperature annealing stage in the *V*-band region. The nature of the centers responsible for this process are not known; however, by analogy with MgO,[15] impurity-cation vacancy complexes or isolated cation vacancies are reasonable candidates. Figure 5(a), curve II which represents the thermal destruction of hole traps shows no substantial change until the temperature exceeds 550 °C indicating that the centers which serve as hole traps are not destroyed in this annealing range.

Curves I and II of Fig. 5(b) record, respectively, the "electronic" and "ionic" isochronal annealing of the 6.1-eV band. As expected curve I falls below curve II with the separation becoming quite substantial above 300 °C. If the 6.1-eV band represented the only trapped electrons, one would expect curve I to reflect in 6.1-eV absorption the first hole release stage exhibited by curve I Fig. 5(a). The absence of such a stage indicates that other occupied electron traps compete effectively for holes. Examination of the difference in absorption spectra in this annealing region reveals that nearly all of the holes released in the first stage are captured by Cr^{2+}. Above 300 °C both electronic and ionic annealing become important. The wide separation between the two curves suggests that thermal destruction of *d* centers is easier if the center is first emptied of its trapped electron either by ionization or by recombination with a free hole. The separation between curves I and II is consistent with earlier observations of Levy[3] on isochronal annealing of much heavier neutron-irradiated Al_2O_3 crystals before and after γ irradiation. The gradual decline of curve II over the range from 300 to 600 °C indicates that the annealing of the neutron damage is a complex affair and not a simple singly activated process.

The annealing of the *d* centers and the related 6.1-eV band seems to occur in these more or less distinct temperature ranges; one prominent stage centered at 300 °C, one small stage near 450 °C, and one above 500 °C. This recovery behavior is markedly different from that observed by Levy[3] which may result from the fact that he employed higher neutron exposures and a higher irradiation temperature than were used in our experiments.

IV. CONCLUSIONS

(i) The correlation between the growth of the V_{OH}^- band and the enhancement of the 6.1-eV band upon γ irradiation of neutron-bombarded Al_2O_3 together with the optical bleaching of both bands by 410-nm excitation are convincing evidence that the 6.1-eV band is associated with electrons trapped at some defect (termed the *d* center) created by atomic displacement.

(ii) Since subsequent γ irradiation caused a substantial enhancement in the 6.1-eV band owing to hole trapping at native defects, it is clear that the amplitude of this band reflects the concentration of trapped holes rather than the *d*-center concentration. In this connection it should be mentioned that increasing the neutron exposure a factor of 10 reduced the enhancement due to a saturation γ irradiation to only 1% to 2%, which is strong indication that, when the native hole-trapping center concentration is small compared to those resulting from the neutron bombardment, the 6.1-eV band reflects mainly the latter.

(iii) The observation that isochronal annealing of the *d* centers occurs gradually over a wide temperature range indicates that in neutron-bombarded crystals annealing of the damage is a complex process. It would be interesting to compare this recovery with that for *d* centers created by electron bombardment in which the damage configuration is of a more simple form.

Although the work presented here does not yield a conclusive identification of the *d* center, the positive clue that this center traps an electron to produce absorption in the 6.1-eV region helps rule out certain possibilities. For example, the Al^{3+} vacancy is eliminated since such a defect would be expected to trap holes rather than electrons. On the other hand, the Al^{3+} interstitial would be a reasonable candidate. In support of this, Cox and Herve[16] and Cox[17] have reported ESR spectra of three different types of paramagnetic off-center aluminum interstitials at least one of which is stable at room temperature. Alternatively, some form of oxygen vacancy might be the *d* center. La *et al.*[18] have detected the ESR spectrum of the F^+ center, i.e., a single electron trapped at an oxygen vacancy in reactor-irradiated Al_2O_3. Although the resonance of these centers has been resolved from the rather complex ESR spectrum only in heavily irradiated crystals (~10^{18} neutrons/cm^2), there is no reason to conclude that they might not be present in appreciable concentration in specimens receiving much lower exposures and even in electron bombarded crystals. Therefore, F^+ centers or possibly F centers should not be discounted as possible candidates at this stage. Clearly additional experimental information is required for conclusive identification of the d center.

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