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Electron spin resonance spectra of Eu^{2+} and Tb^{4+} ions in glasses

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Abstract. Electron spin resonance (ESR) spectra of Eu^{2+} and Tb^{4+} were observed at room temperature in one fluoride phosphate and two phosphate glasses. Although both ions are isoelectronic, they have different ESR spectra. Eu^{2+} ions exhibit pronounced features at effective g -values of 2.0, 2.8 and 6.0, which is typical for the so-called U-spectrum. Tb^{4+} ions give only a single feature at $g = 5.0$. The different spectra are due to different crystal field strengths. The higher charge of Tb^{4+} ions results in a stronger local field compared with Eu^{2+} ions.

1. Introduction

Rare earth (RE) ions occur predominantly in the trivalent state in glasses. Because of their electron configurations, europium and terbium ions can exist in other valencies, too. Eu^{3+} requires one electron for the stable half-filled 4f shell. Thus, it can be reduced to Eu^{2+} . On the other hand, Tb^{3+} has one electron above the half-filled 4f shell. Therefore, it can be oxidized to Tb^{4+} .

The absorption and emission properties of Eu^{2+} are attractive for Faraday rotators and phosphors [1, 2]. The photooxidation of Eu^{2+} under irradiation in the ultraviolet (UV) spectral region is responsible for their growing interest in Bragg gratings and persistent spectral hole burning [3, 4]. Both effects are the basis of new photonic elements [5, 6]. The capability of both europium and terbium ions to change their valencies makes these ions suitable indicators for investigation of radiation-induced defect centre formation in glasses. Further, it affects the sensitivity or resistance of glasses against irradiation [3, 7].

Electron spin resonance (ESR) spectroscopy is an useful tool for detection of ions and for determination of the environment around ions. Reliable ESR spectra of RE ions in glasses have been reported almost solely for the two $4f^7$ ions, Eu^{2+} and Gd^{3+} [8–13]. They have an orbital singlet $^8S_{7/2}$ ground term, i.e. the orbital angular momentum is zero. In the case of non-S-state ions, low-lying excited states resulting from the minimal quenching of orbital motion give rise to exceedingly short relaxation times (leading to enormous linewidths at practical laboratory temperatures) and large spectral anisotropies (which particularly smear out spectra observed in glasses) [14].

Tb^{4+} is isoelectronic with Eu^{2+} and Gd^{3+} . Tb^{4+} ESR spectra have been observed in crystals [15, 16]. But to the best knowledge of the authors, no Tb^{4+} ESR spectra have been reported in glasses. Since Tb^{4+} is an S-state ion like Eu^{2+} and Gd^{3+} , we expect quite narrow ESR features for Tb^{4+} ions in glasses as observed for Eu^{2+} and Gd^{3+} .

In this paper, we report ESR spectra of Eu^{2+} and Tb^{4+} ions in fluoride phosphate and phosphate glasses which are attractive materials for rare earth doped photonic elements [17, 18] and high performance optics [19]. Eu^{2+} ions were obtained by reducing melting conditions. Tb^{4+} ions were formed under x-ray irradiation. ESR spectroscopy is shown to be a suitable method for controlling the formation of these ions. Although Eu^{2+} and Tb^{4+} ions are isoelectronic, they exhibit different ESR spectra, which suggests different crystal fields around these ions.

2. Experiment

2.1. Preparation of glass samples containing Eu^{2+} and Tb^{4+} ions

A fluoride phosphate (FP) glass, a sodium–strontium–metaphosphate (NSP) glass and a multicomponent ultraphosphate (UP) glass were used as host materials for the RE ions. The batch compositions of the host glasses are given in table 1. The FP glass was doped with EuF_3 and TbF_3 , respectively. The two phosphate (P) glasses were doped with Eu_2O_3 and Tb_4O_7 , respectively. The concentrations of the RE ions in the batches are reported in table 1.

Table 1. Batch composition of the glasses investigated.

| Glass type | Glass | Batch composition (mol%) | RE concentration (10^{19} ions cm^{-3}) |
|------------|-------|---|--|
| FP | FP | 10 $\text{Sr}(\text{PO}_3)_2$ –10 MgF_2 –30 CaF_2 –15 SrF_2 –35 AlF_3 | 1 |
| P | NSP | 33 NaPO_3 –66 $\text{Sr}(\text{PO}_3)_2$ | 6 |
| | UP | 65 P_2O_5 –3 MgO –9 CaO –10 ZnO –9 BaO –4 Al_2O_3 | 1 |

Raw materials of high purity suitable for optical glasses were used. The FP glass samples were melted from fluorides and $\text{Sr}(\text{PO}_3)_2$. The UP glass samples were prepared from oxides and carbonates. The NSP glass samples were obtained from NaPO_3 and $\text{Sr}(\text{PO}_3)_2$ containing comparatively high amounts of organic impurities with respect to the raw materials used for melting the FP and UP glass samples.

Reducing melting conditions were employed to obtain Eu^{2+} ; x-ray irradiation was used to obtain Tb^{4+} in the glasses. The occurrence of these ions was detected by optical spectroscopy as described in [20].

At first, samples were melted from batches in air using platinum crucibles for the FP glasses and silica glass crucibles for the P glasses. No Eu^{2+} ions were detected in the FP and UP glasses melted in air. In the FP glass, Eu^{2+} ions were obtained under reducing conditions by remelting of the starting glasses in carbon crucibles in argon atmosphere. In the UP glass, no Eu^{2+} ions were found despite the use of different reducing conditions such as remelting of the starting glasses in carbon crucibles or addition of sugar and aluminium powder to the batches. Therefore, we examined the NSP glass melted in air in which a small amount of the comparatively high Eu^{3+} content in the batch was reduced to Eu^{2+} due to the short melting time and the reducing effect of the organic impurities in the raw materials.

Tb^{4+} ions could not be formed in glasses by oxidizing melting conditions using oxygen bubbling. However, irradiation with x-rays and UV light is known to produce Tb^{4+} in glasses [21–23]. In both FP and UP glasses, Tb^{4+} ions were obtained by irradiating samples with the unfiltered radiation of a Cu-cathode x-ray tube working at 50 kV and 160 mA.

The glasses melted in platinum and silica crucibles were poured into graphite moulds and then slowly cooled to room temperature. The glasses melted in carbon crucibles were first rapidly cooled in the crucibles to about 800 K and then slowly cooled to room

temperature. All glasses prepared are transparent and have an optical quality suitable for optical measurements such as transmission spectroscopy.

2.2. ESR measurements

The ESR measurements were carried out at X-band frequency (9.8 GHz) at room temperature. All spectra were recorded under the same conditions (accumulation, intensification). Therefore, different signal-to-noise ratios reflect different concentrations of the RE ions which cause the spectra. In the case of FP and UP glasses, bulk samples were measured. In the case of NSP glass, a powder sample obtained by cracking and crushing glass pieces in a mortar was used. Glass powdering in such a way does not lead to crystallization of glasses.

3. Results and discussion

In the ESR spectra of both Eu^{2+} containing glasses, pronounced features are observed at effective g -values of 2.0, 2.8 and 6.0. Weaker features are found at $g = 3.4$ and 4.5 (figure 1). The shape of the spectrum equals the so-called U-spectrum found for Gd^{3+} and Eu^{2+} in different glass types [8–13].

The sharp resonances at about $g = 2$ in the NSP glass are due to Mn^{2+} ions. In glasses, Mn^{2+} gives rise to a pronounced feature at about $g = 2$ which is split into six ESR signals as a result of hyperfine splitting [24]. Beside the europium doped NSP glass, this sextet is also observed in the undoped FP and UP glasses. However, the intensity of the sextet is very low, because the glasses contain only <1 ppm manganese which is introduced by the raw materials [25]. The Eu^{2+} content in the FP and UP glasses is considerably larger (>100 ppm) than the one of Mn^{2+} . Therefore, the weak Mn^{2+} signals are not resolved beside the intense Eu^{2+} signal at $g = 2.0$. The Eu^{2+} content of the NSP glass is in the range of 10 ppm and thus clearly lower than the one in the FP and UP glasses. Therefore, the weak Mn^{2+} signals are observable in the NSP glass beside the Eu^{2+} signal.

The ESR spectra of both Tb^{4+} containing glasses after irradiation are shown in figure 2. The intense features in the range of $g = 1.7$ – 2.7 are found in both terbium doped and undoped glasses only after irradiation with UV light or x-rays. They are caused by intrinsic defect centres formed by irradiation in the FP and UP glasses [23, 26]. The positions and splittings of the intense features are consistent with ESR spectra of radiation-induced defect centres in phosphate containing glasses described by several authors [26–28]. The single feature at $g = 5.0$ is solely observed in the terbium doped glasses after irradiation. In these glasses, radiation-induced Tb^{4+} ions were detected by absorption spectroscopy [20]. Since the ESR feature at $g = 5.0$ correlates with the Tb^{4+} absorption and since Tb^{4+} ions are expected to exhibit observable ESR features in glasses at room temperature as explained above, the feature at $g = 5.0$ is assigned to Tb^{4+} ions. The intense features of the intrinsic defect centres ($g = 1.7$ – 2.7) exhibit no difference in terbium doped and undoped samples. This suggests that no pronounced Tb^{4+} features exist in the range of the defect centre features.

Considering the prominent feature of Eu^{2+} at $g = 6.0$ and the one of Tb^{4+} at $g = 5.0$, the signal-to-noise ratios are clearly different for the two RE types in the case of the FP glass as well as for the two glass types in the case of one RE type (figures 1 and 2). All the differences in the signal-to-noise ratios result from differences in the Eu^{2+} and Tb^{4+} concentrations in the glass matrices. Under x-ray irradiation, only a fraction of the Tb^{3+} ions is converted into Tb^{4+} ions. The efficiency of the irradiation to form Tb^{4+} is different in the two glass types. From absorption spectra, we estimate that 5–7% of the Tb^{3+} ions in the FP glass are converted into Tb^{4+} ions, whereas this part amounts 10–12% in the case of the UP glass. The higher amount of

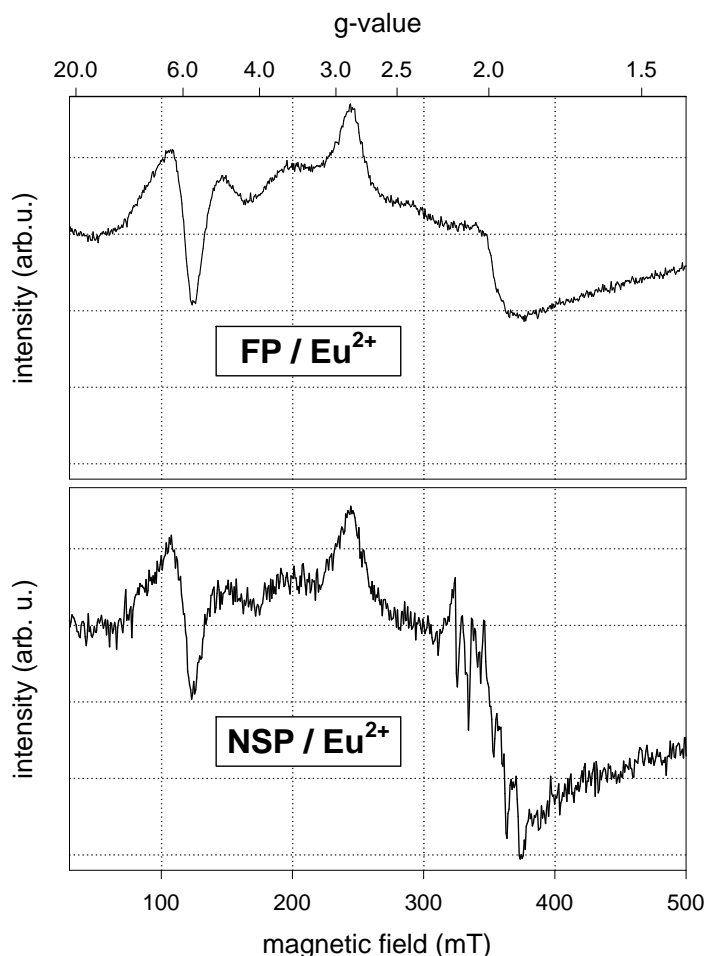


Figure 1. X-band ESR spectra of Eu^{2+} containing FP and NSP glass.

Tb^{4+} ions in the UP glass compared with the FP glass is consistent with the lower signal-to-noise ratio of the ESR spectrum of Tb^{4+} in the UP glass. Similar to the formation of Tb^{4+} ions under irradiation, the formation of Eu^{2+} ions by the use of reducing melting conditions is incomplete. It is noted that the Eu^{3+} and Tb^{3+} concentrations in the FP glass before the use of reducing melting conditions and irradiation, respectively, are equal. Comparing Eu^{3+} fluorescence spectra of FP glasses melted in air and melted under reducing conditions, 30–70% of the Eu^{3+} ions are estimated to be converted into Eu^{2+} ions. This amount is clearly higher than the 5–7% of the Tb^{3+} ions which are converted into Tb^{4+} ions. This result explains the clearly lower signal-to-noise ratio of the Eu^{2+} ESR spectrum compared with the Tb^{4+} ESR spectrum in the case of the FP glass. The higher signal-to-noise ratio of the Eu^{2+} ESR spectrum in the NSP glass with respect to the FP glass is due to lower Eu^{2+} content in the NSP glass as mentioned above.

Eu^{2+} and Tb^{4+} ions give rise to different ESR spectra in the glasses investigated, although both ions are isoelectronic. The Eu^{2+} ESR spectra are similar to the well known U-spectrum having several features at effective g -values in the range of 2 to 6. By contrast, the ESR Tb^{4+} spectra consist of a single feature at an effective g -value of 5.0. This difference in the ESR

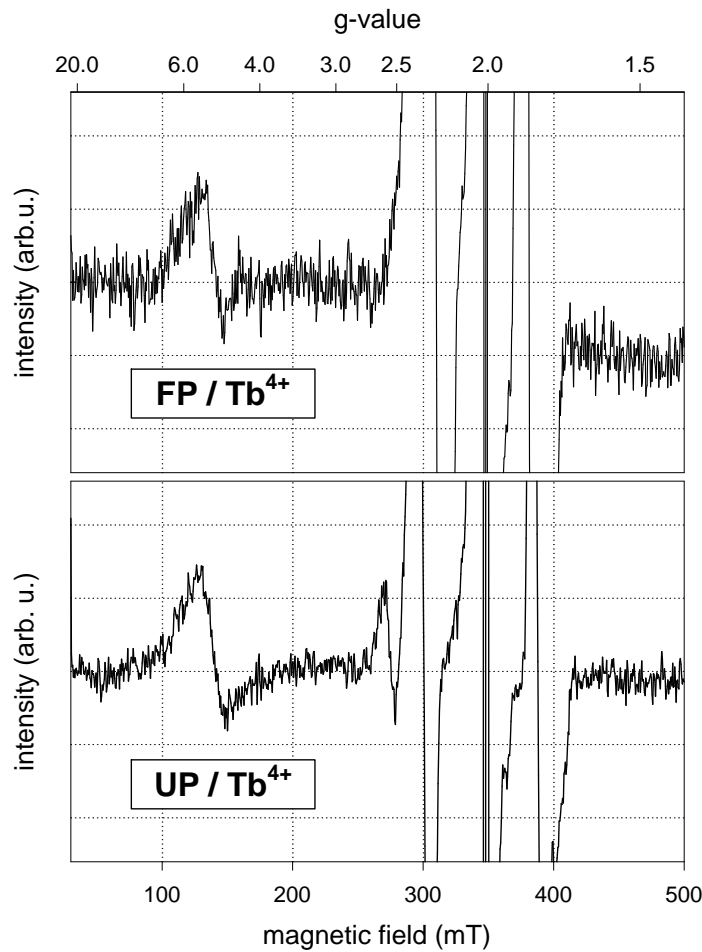


Figure 2. X-band ESR spectra of Tb^{4+} containing FP and UP glass, recorded after x-ray irradiation.

spectra of Eu^{2+} and Tb^{4+} ions are attributed to different crystal field strength around these ions in the glasses investigated for the following reasons.

For the $4f^7$ ions, Eu^{2+} , Gd^{3+} and Tb^{4+} , with the free ion ground term $^8S_{7/2}$, the spin Hamiltonian which incorporates Zeeman and crystal field (CF) interactions is given by

$$H = H_{\text{Zeeman}} + H_{\text{CF}} \quad (1)$$

which for the case of operators up to second order in the spin may be written as

$$H = g_0 \beta \mathbf{B} \cdot \mathbf{S} + 1/3(b_2^0 O_2^0 + b_2^2 O_2^2) \quad (2)$$

where $g_0 = 2.00$, β is the Bohr magneton, \mathbf{B} is the applied magnetic field, $S = 7/2$ and the spin operators O_2^q have their corresponding CF parameters b_2^q [10]. All physically distinct CF symmetries ranging from axial to fully rhombic are described by the asymmetry parameter $\lambda' = b_2^2/b_2^0$ in the range $0 \leq \lambda' \leq 1$.

In the dependence of the magnitude of the CF splitting, H_{CF} , on the applied microwave frequency, ν , different types of ESR spectrum are distinguished [10]. In the weak category, $H_{\text{CF}}/h\nu \leq 1/4$, an ESR spectrum results primarily from first-order transitions between

Zeeman levels as weakly perturbed by H_{CF} . Hence, the spectrum is primarily concentrated in the vicinity of $g \sim 2$. In the intermediate CF category, $1/4 \leq H_{CF}/h\nu \leq 4$, an ESR spectrum generally consists of many resonances, the majority of which have effective g -values > 2 . The preponderance of $g > 2$ resonances results from first-order transitions that are shifted to $g > 2$ by H_{CF} and higher-order transitions that extend between the various Kramers levels most often at low field ($g > 2$) and which are now allowed by H_{CF} . In the strong CF category, $H_{CF}/h\nu \geq 4$, the ESR spectrum is entirely controlled by those few resonances resulting from transitions within the Kramers levels. The angular dependence and transition probability of those few resonances are such that only a small number of prominent features with $g > 2$ appears in the spectra of samples containing randomly oriented paramagnetic ions.

Brodbeck and Iton [10] have made a complete reconstruction of the U-spectrum of Gd^{3+} in glassy and polycrystalline silicate hosts by computer simulations assuming the intermediate CF category. The simulations showed that the U-spectrum is the result of: (a) a broad distribution of b_2^0 values with a maximum in the range of $0.051 \lesssim b_2^0 \lesssim 0.056 \text{ cm}^{-1}$ and (b) a broad and slowly varying λ' distribution with appreciable probability over the whole range $0 \leq \lambda' \leq 1$. These results indicate that the site symmetries of the RE ions are essentially very low and disordered [10]. Legein *et al* [13] confirmed by multiband ESR spectra of Gd^{3+} in fluoride glasses that b_2^0 is in the range of $0.02 \lesssim b_2^0 \lesssim 0.15 \text{ cm}^{-1}$, which substantiates the validity of the intermediate CF category for the U-spectrum at X-band frequency. By computer simulations of X-band ESR spectra of Gd^{3+} in fluoride glasses, Furniss *et al* [11] and Legein *et al* [13] determined average b_2^0 values in the range of $0.06 \lesssim b_2^0 \lesssim 0.09 \text{ cm}^{-1}$, which is similar to the range of average values determined by Brodbeck and Iton for Gd^{3+} in glassy and polycrystalline silicate hosts (see above). It is interesting to note that Legein *et al* [13] improved the computer simulations of Brodbeck and Iton [10] by using a distribution of b_2^0 and λ' , which yields zero probability for $\lambda' = 0$ ($0.6 < \lambda' < 1$). From a structural point of view, this solution is more plausible. Zero probability for $\lambda' = 0$ indicates that the existence of high-symmetry polyhedra is prohibited, which is in agreement with the notion of disorder generally considered in glasses.

Multiband ESR spectra of Gd^{3+} and Eu^{2+} in glasses demonstrate that at lower-frequency bands compared with the X-band the most conspicuous sharp feature at $g \approx 6.0$ of the U-spectrum gradually vanishes and another broader feature at $g \approx 5.0$ arises [12, 13]. In the case of Eu^{2+} in SiO_2 - Al_2O_3 glass at microwave frequencies $\nu \leq 4.6 \text{ GHz}$ and in the case of Gd^{3+} in phosphate glasses at $\nu \leq 3.5 \text{ GHz}$, the $g \approx 5.0$ feature predominates and no features having lower g -values occur. A decrease of the microwave frequency shifts ESR spectra into the strong CF category. In this category, an ESR spectrum is controlled by the few resonances *within* the Kramers levels. Nicklin *et al* [8] and Čugunov *et al* [12] assigned the $g \approx 5.0$ feature to transitions within the second-lowest Kramers doublet. This suggests that the lower-frequency ESR spectra consisting solely of a single $g \approx 5.0$ feature belong to the strong CF category.

In some solids, a pronounced feature at about $g = 5$ is observed in Gd^{3+} and Eu^{2+} ESR spectra already at X-band frequency. This feature behaves independently of the U-spectrum. The ESR spectrum of Gd^{3+} in pure silica glass without modifier oxides consists only of a sharp feature at $g = 5.0$ [8]. Eu^{2+} gives rise to an intense signal at $g = 4.9$ in some zeolites [29]. By calculations in the strong CF category, Nicklin *et al* [8] demonstrated that there is an isotropic resonance at $g = 5.0$ for $\lambda' = 0.36$. In the case of Eu^{2+} doped zeolites, Iton and Turkevich [29] attributed the $g = 4.9$ signal to sites causing large CF splitting, whereas the U-spectrum is characteristic for sites causing medium CF splitting as described above. The attribution of the $g = 5$ feature to high CF strength is substantiated by optical properties of RE ions in silica glass. Exceptionally high CF strength of RE^{3+} sites was identified for this glass in contrast

to many other glass types by absorption and luminescence spectroscopy [17]. This coincides with the observation that only a single $g = 5$ feature occurs in the X-band ESR spectrum of Gd^{3+} in silica glass.

The ESR spectra of Tb^{4+} in FP and UP glasses at X-band frequency resemble those of Eu^{2+} in $\text{Al}_2\text{O}_3\text{-SiO}_2$ glass at lower-frequency bands ($\nu \leq 4.6$ GHz) [12] as well as that of Gd^{3+} in pure silica glass [8]. According to the isospectral frequency ratio method [12], the coincidence of the Tb^{4+} spectra with the Eu^{2+} spectra at a higher frequency compared with the Eu^{2+} spectra indicates higher CF strength for Tb^{4+} sites in FP and UP glasses compared with Eu^{2+} sites in $\text{Al}_2\text{O}_3\text{-SiO}_2$ glass. Since the lower-frequency Eu^{2+} spectra as well as the X-band Gd^{3+} spectrum in pure silica glass are attributed to the strong CF category, the similarity of the Tb^{4+} spectra with these spectra suggests the validity of the strong CF category also for the X-band Tb^{4+} spectra. In summary, the applied microwave frequencies of the single $g \approx 5$ feature spectra for different RE ions and different glass types [8, 12] demonstrate that the CF strength of the RE sites increases in the order: Gd^{3+} in phosphate glasses $< \text{Eu}^{2+}$ in $\text{Al}_2\text{O}_3\text{-SiO}_2$ glass $< \text{Gd}^{3+}$ in SiO_2 glass $\approx \text{Tb}^{4+}$ in FP and UP glasses.

According to the interpretations of Eu^{2+} , Gd^{3+} and Tb^{4+} ESR spectra given above, two types of spectra and RE sites are distinguished. At a fixed microwave frequency, the single $g = 5$ feature spectrum is observed in the case of large CF splitting of the RE sites, whereas the U-spectrum having many resonances is found at smaller CF splitting. Thus, the U-spectrum of Eu^{2+} and the single feature spectrum of Tb^{4+} observed at X-band frequency in the FP and UP glasses indicate higher CF strengths around Tb^{4+} ions compared with Eu^{2+} ions. This result agrees with the general tendency that the CF strength increases with increasing charge of the metal ions [30] and is substantiated by the extremely large CF splitting found for Tb^{4+} in crystals [16].

4. Summary and conclusions

ESR spectra of Eu^{2+} and Tb^{4+} ions were recorded in FP and P glasses. Eu^{2+} and Tb^{4+} ions were obtained by reducing melting conditions and by x-ray irradiation, respectively. ESR spectroscopy is found to be a suitable method for detection of these ions. Although Eu^{2+} and Tb^{4+} ions are isoelectronic, they exhibit different X-band ESR spectra in FP and P glasses. This is due to higher crystal field strengths around Tb^{4+} ions because of higher charge of Tb^{4+} ions compared with Eu^{2+} ions.

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