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Abstract. The O K-edge x-ray absorption near edge structure (XANES) spectrum of UO_2 is presented and interpreted. A comparison with that corresponding to CeO_2 is made. First-principles-based calculations using the LSDA+U approach allows us to link each feature present in the spectra to the specific atomic arrangement and electronic structure of the compound. The structures at the edge originate from oxygen 2p states hybridized with U 5f and 6d orbitals and the 6d e_g–t_{2g} splitting is found to be 4.8 eV. The structures due to O 2p–U 5f hybridization are found to be lower in energy than the structures due to the O 2p–U 6d hybridization. On this basis, UO_2 can be considered as an f–f Mott–Hubbard insulator.

1. Introduction

Uranium dioxide is an important technological material mainly used as fuel in nuclear power plants that has been widely studied, especially from a chemical and thermodynamical point of view [1]. Its electronic structure has been investigated by x-ray and resonant photoelectron spectroscopies (XPS [2, 3] and RPS [4]), which concern the occupied states, and by optical absorption [5], bremsstrahlung isochromat spectroscopy (BIS) [2], inverse photoemission [6] and x-ray absorption spectroscopy (XAS) [7, 8], which concern the empty states.

In spite of all these experimental results, as well as theoretical ones [3, 9–12], several important points about the electronic structure of UO_2 are still debated: while it has been well established that the satellites that appear in the 4f XPS spectrum come from strong hybridization in the final state [3, 9], the strength of the O 2p–U 5f hybridization has been assumed to be zero [11], to exist [13] or to be strong [3] in preceding papers. The nature of the insulating state in the ground state also remains controversial: although it seems to be confirmed that UO_2 is a Mott–Hubbard insulator, it is not clear however whether it is a 5f–6d [3] or a 5f–5f [9] one.

In this paper, we tackle these unresolved questions, discussing the electronic structure of UO_2 in the light of new experimental results at the x-ray absorption O K edge, interpreted thanks to first-principles calculations in the frame of the LSDA + U approach. Indeed, if there is a covalent bonding between oxygen and uranium ions, this means that charge transfer has occurred from O^{2-} to U^{4+}; the O 2p orbitals have therefore an empty antibonding part

due to hybridization with U empty orbitals, that is likely to be investigated in an O K XANES experiment, as it involves a 1s–2p electronic transition, according to the dipole selection rules.

In this paper, we focus on the structures that are close to the edge; the second part of the spectrum will be discussed in a forthcoming paper. This paper is organized as follows: the experimental part, including sample preparation, experimental details and results, is presented in section 2 while section 3 is devoted to the presentation of the calculations. Section 4 deals with the interpretation of the results in terms of anion–cation hybridization. General tendencies concerning the electronic structure of UO_2 are discussed at the end of the paper.

2. Experimental details

Uranium and cerium dioxides crystallize in the fluorite structure (CaF_2) and belong to the $Fm3m$ space group. The unit cell parameter is $a = 5.47$ Å for UO_2 and 5.40 Å for CeO_2. The lattice can be described as an fcc cation lattice in which all the tetrahedral sites are occupied by an oxygen atom. This leads to a cubic local symmetry around each cation (eight oxygen neighbours located at 2.37 Å in UO_2 and 2.34 Å in CeO_2).

In our experiments, we have used a polycrystalline mechanically polished UO_2 sample: the UO_2 powder was sintered (at 2000 K for 5 h) under hydrogen atmosphere. The stoichiometry ($UO_{2.00}$) has been checked by thermogravimetry and the unit-cell parameter by x-ray diffraction. Prior to the XAS experiments, an XPS spectrum was obtained and is found to be similar to the results of [14], after a very slight ion etching (argon ions, 2 keV, 10 μA, 1 min) to get rid of surface carbon contamination.

X-ray absorption experiments were carried out on the SA22 beam line of the Super ACO storage ring at the LURE synchrotron facilities (Orsay, France). A plane grating monochromator (PGM, 12 m) produces an incident photon beam with energies ranging from 80 eV to 900 eV. The total electron yield I was measured by a channeltron placed in front of the irradiated sample. The primary photon beam intensity I_0 was monitored by a second channeltron, which measured the total electron current from a gold grid located in front of the analysis chamber in the path of the photon beam. The I/I_0 ratio was measured as a function of photon energy, ranging from 520 to 580 eV, with a resolution of 0.3 eV.

The spectra of the UO_2 sample obtained from total yield detection can confidently be considered as reference spectra for the said material, since the x-ray absorption spectroscopy (XAS) sampling depth, which we estimate to be ∼100–200 Å [15], is large enough to eliminate any significant contribution from the outermost layers, including contaminants.

The sample preparation and the experimental conditions for CeO_2 have been already given in [16].

Oxygen K-edge spectra of UO_2 and CeO_2 are shown in figure 1. We can distinguish two parts in these spectra: the first one, up to 540 eV, called the edge region, displays four main features labelled a, b, c and d for UO_2 and three for CeO_2 (labelled b, c, d). The second part, beyond 540 eV, presents five visible structures labelled A, B, C, D and E. Their energy positions are listed in table 1.

3. Calculation details

The calculations have been performed starting from the framework of the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA) [17]. As already
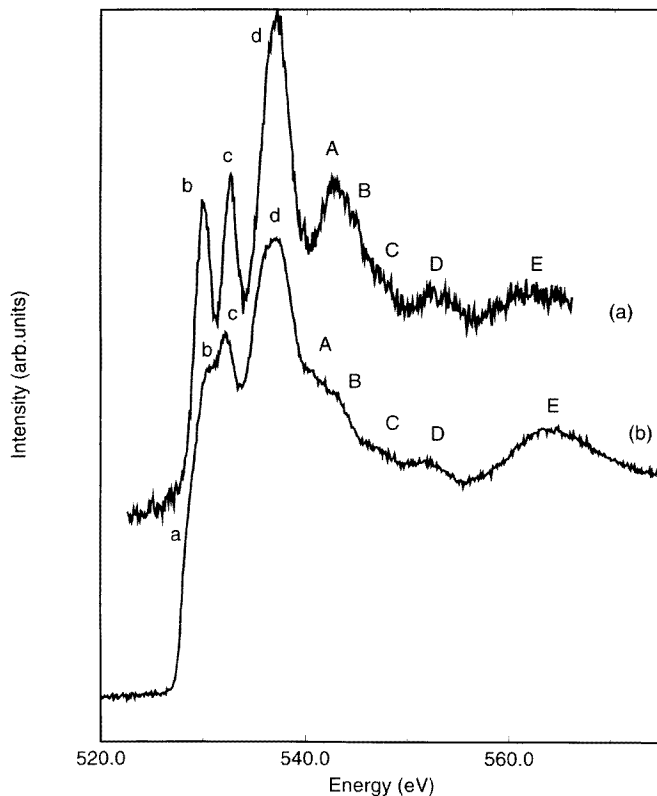
Figure 1. XAS oxygen K edge of CeO$_2$ (a) and UO$_2$ (b).

Table 1. Energies of the structures of the O K XAS spectrum for CeO$_2$ and UO$_2$.

	a	b	c	d	A	B	C	D	E
CeO$_2$ (eV)	—	530.9	533.5	537.9	543.6	545.7	548.7	553.9	563.4
UO$_2$ (eV)	528.55	530.65	532.2	537.0	540.9	543.1	546.85	551.85	564.05

shown [12], the ground state of UO$_2$ calculated using this code is found to be metallic, contrary to experimental findings [2]. To overcome this difficulty, we have followed the suggestion of Anisimov *et al* [18] by adding an orbital-dependent correction to the local density approximation (LDA) potentials, the so-called LDA $+ U$ method where U is an on-site Coulomb interaction. According to [18], this implies a correction to the potential acting on an f electron that can be written

$$\delta V_{im\sigma} = (U - J)(\tfrac{1}{2} - n_{im\sigma})$$

where i, m and σ label respectively the uranium site, the f orbital and the spin of the f electron. U and J are the Coulomb and exchange interaction between electrons, and n is the orbital occupation number. This correction, valid for a spin-dependent LDA calculation (LSDA), has been included in the computational code. For the calculations the values $U = 4.5$ eV and $J = 0.54$ eV have been used, following previous theoretical calculations

[9]. They are in good agreement with the experimental determination of U presented in [2]. To validate our LSDA $+ U$ correction, we have checked we obtained a good agreement with the recent results of Dudarev *et al* [19]. As expected, an insulating ground state is reached for the antiferromagnetic phase, as well as for the paramagnetic one. As the aim of this calculation is to interpret the experimental XAS O K edge in UO_2, that was obtained at room temperature, we have performed the calculations in the paramagnetic state. As there are many ways to put the two uranium f electrons into the different f orbitals, we have checked that the calculated density of states (DOS) did not depend on this choice: only very tiny differences in the DOS shapes have been found, so that the physical conclusions we draw from this calculation do not depend on the initial paramagnetic state we have chosen. The result of the calculation is shown in figure 2: the U 5f, U 6d and O 2p projected DOSs, that are useful for this paper, are displayed, respectively, in figure 2(a)–(c). The zero of energy is the Fermi level. Only the highest occupied states are shown as we are interested in unoccupied states for this paper. In figure 3, the beginning of the experimental x-ray absorption O K edge spectrum of UO_2 (figure 3(i)) is compared with the calculated O 2p empty density of states (figure 3(ii)). The latter is obtained as follows: rather than starting from the derivative of the number of states to calculate the density of states, as done to obtain figure 2, we have started from the eigenstates of the Hamiltonian, i.e. the eigenvalues associated with the weight of the O 2p states. On these states, a Lorentzian broadening (0.2 eV) has been applied to take into account the core hole lifetime, and a convolution with a Gaussian function (0.35 eV) has been performed to account for experimental broadening. The four experimental structures (a–d) are reproduced by the calculation: as concerns the position of the peaks, the agreement is good, except for peak c which is 0.9 eV lower than on the experimental spectrum. As concerns the intensity of the peaks, the agreement is correct if one keeps in mind that no inverse tangent function has been added to the calculated curve to account for the edge jump.

4. Discussion

Starting from an ionic *ansatz*, UO_2 is formed of U^{4+} and O^{2-} ions. The ionic ground state configuration is therefore written U $6p^6 5f^2 6d^0 7s^0$ O $2p^6$ (reduced notation $5f^2$). When hybridization is switched on, the ground state becomes a mixing of $5f^2$, $5f^3 \underline{L}$ and $5f^2 6d^1 \underline{L}$ configurations ($\underline{L}$ denotes an oxygen ligand 2p hole). Only one ligand hole has been taken into account in this description. Configurations involving the 7s states have been neglected since they are supposed to be higher in energy [20]. During the oxygen K edge XAS process, an oxygen 1s electron is promoted to the oxygen empty 2p levels in the frame of the electric dipolar approximation. This means that the lowest-energy final states reached after absorption are a mixture of the $|\underline{c}_O 5f^3\rangle$ and $|\underline{c}_O 5f^2 6d^1\rangle$ ones ($\underline{c}_O$ denotes a 1s oxygen hole). The mixing is due to non-diagonal 5f–6d electronic interactions: as these latter are expected to be small (the corresponding Slater integrals are in the range 1–3 eV [20]), we can consider that the final-state configurations will be made of two types of configuration, one with a great weight on the $|\underline{c}_O 5f^3\rangle$ configurations and another with a great weight on the $|\underline{c}_O 5f^2 6d^1\rangle$ ones. The oxygen K edge XAS spectrum therefore reflects the hybridized part of uranium $5f^3$ and $5f^2 6d^1$ configurations, modulated by the 1s oxygen core hole attraction. The latter however is not of crucial importance here because it is screened by the oxygen 2p full-band electrons. This allows us to use the calculated O 2p-projected DOS to interpret the experimental XAS O K spectrum. In the same way, as CeO_2 is a $4f^0$ compound in the ionic picture, its oxygen K-edge XAS spectrum should reflect the hybridized part of cerium $4f^1$ and $4f^0 5d^1$ configurations.
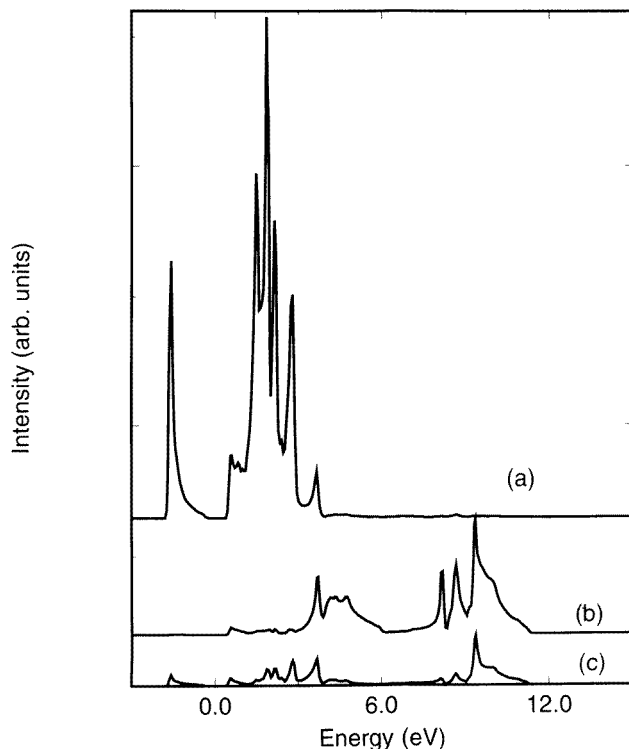
Figure 2. Calculated DOS in UO$_2$ in the frame of an LSDA + U approach: U 5f projected DOS (a); U 6d projected DOS (b); O 2p projected DOS (c). The zero of energy is the Fermi level.

Let us consider first the $5f^2 6d^1$ configurations in UO$_2$. In a cubic crystal field, the d orbitals are split into two sets of orbitals, the e_g ones (two orbitals at lower energy) and the t_{2g} ones (three orbitals at higher energy). Neglecting for the moment spin–orbit coupling and f–d interactions, there are no d multiplet interactions when there is only one d electron, and two types of configuration are to be taken into account: the $5f^2 6e_g^1$ and the $5f^2 6t_{2g}^1$ ones to which we attribute respectively the peaks c and d. Indeed, as shown in figure 2, the U 5f states in the conduction band (figure 2(a)) are lower in energy than the U 6d states (figure 2(b)), although there is a small overlap between the f states and the e_g ones. When considering the O 2p-projected DOS, the structures coming from the hybridization between U 5f and O 2p states are therefore lower in energy than the ones coming from a U 6d–O 2p hybridization (figure 2(c)). The energy difference between peaks c and d measured on the experimental spectrum is 4.8 eV, which is to be compared with the 5.7 eV difference between the 2p–e_g and 2p–t_{2g} hybridized states on the calculated O 2p-projected DOS. Within a multiple scattering approach, Guo *et al* [7] found a value of the 4.4 eV. This assignment of peaks c and d is consistent with previous experimental results on the oxygen K edge in other d^0 cubic compounds (ZrO$_2$, HfO$_2$ and CeO$_2$): for ZrO$_2$ and HfO$_2$, in which the cation has nearly cubic coordination, the oxygen K edge shows two sharp peaks, attributed to oxygen 2p states hybridized with cation e_g and t_{2g} states split by the crystal field ([21], see also [22]). In CeO$_2$, the oxygen K edge is made up of three sharp peaks [16]. The first one (b in figure 1) has been attributed to oxygen 2p states hybridized
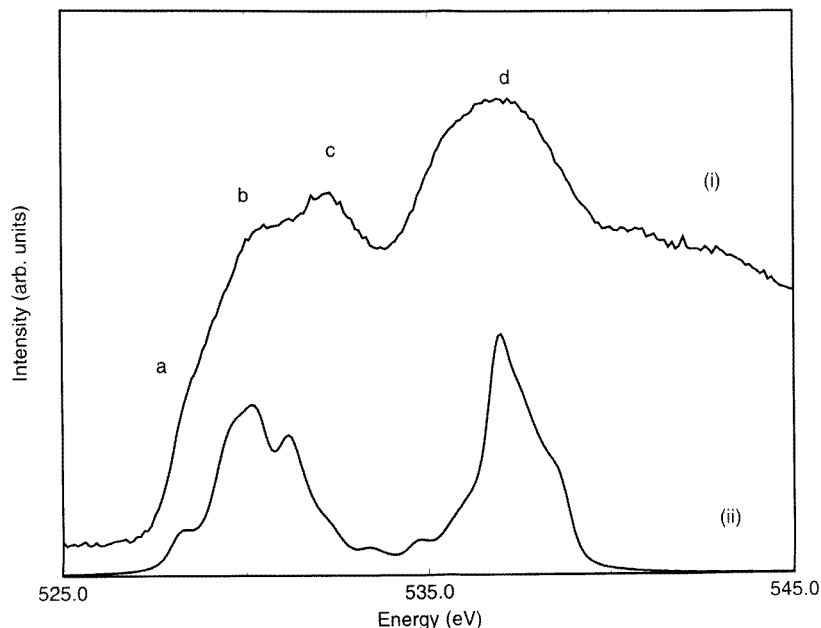
Figure 3. Experimental XAS oxygen K edge of UO_2 (i) compared with the O 2p calculated DOS; (ii) (see text for explanations).

with Ce 4f states. The two following ones (c and d in figure 1) are separated by 4.3 eV, a value which is in good agreement with the 4 eV e_g–t_{2g} splitting value found theoretically [23].

The value of the 6d splitting (4.8 eV) found from the experimental O K XAS spectrum of UO_2 is nevertheless in conflict with previous optical data [5] that predict a 2.8 eV splitting of the 6d orbitals. However, the final state in optical absorption is very different from XAS at the oxygen K edge: whereas the latter involves the $\underline{c}_05f^26d^1$ configurations (for the d states), the optical absorption final state is a mixing of $5f^16d^1$, $5f^26d^1\underline{L}$ and $5f^16d^2\underline{L}$ configurations (if we restrict ourselves to one ligand hole) that leads to different final state energies.

It is difficult to discuss the intensities and widths of the peaks c and d, as they overlap with the other structures (a and b on the lower-energy side, A and B on the high-energy one). It is however clear that peak d is more intense and wider than peak c. As already mentioned by de Groot *et al* [22] several effects must be considered to account for the relative intensities of peaks c and d: one can first consider that peak intensities are related to the number of 6d holes in uranium, modulated by the hybridization effects. Indeed in a cubic crystal field, there are two e_g and three t_{2g} 6d orbitals in uranium. Without hybridization, a ratio of 2:3 for the peak intensities is therefore expected. As the O 2p–t_{2g} hybridization is stronger than the O 2p–e_g one, a more intense t_{2g} peak is expected, as can be seen in figure 1. We have to consider also other effects that may be involved in the peak widths and intensities and that have been neglected up to now. The first one is the spin–orbit splitting of the 6d electrons that is estimated to be ~0.6 eV [24]. Although small compared to the 4.8 eV splitting experimentally observed, this value is not negligible so spin–orbit coupling may lead to a peak broadening. The same conclusion can be drawn

if the f–d electronic interactions are considered: multiplet 5f–6d splitting, added to the 6d spin–orbit splitting, may also contribute to configuration interactions in the final state being more complex than the simple e$_g$–t$_{2g}$ picture.

We consider now the 5f^3 configurations in UO$_2$. We attribute the structures a and b to the O 2p states hybridized with the 5f^3 ones. Indeed, we have already seen that the calculated U 5f states were lower in energy than the U 6d ones (cf figure 2). This can be also established as follows: considering the paramagnetic phase and neglecting the spin–orbit coupling and the multiplet structure for the moment, the energy of the 5f^3 and 5f^{2}6d(e$_g$)^1 configurations can be written $E(5f^3) = 3\varepsilon_f + 3U_{ff} - J$ and $E(5f^2 6d^1) = 2\varepsilon_f + \varepsilon_d + U_{ff} + 2U_{fd}$, where ε_f and ε_d are the f and d orbital energies without electronic interactions, and U_{ff}, J and U_{fd} are respectively the mean 5f–5f Coulomb and exchange interactions and the mean 5f–6d Coulomb interactions. From [9], we take $U_{ff} = 4.5$ eV and $J = 0.5$ eV and $\varepsilon_v - \varepsilon_f = 1.5$ eV (with ε_v the energy of a 2p oxygen electron). From [2], we take $\varepsilon_d - \varepsilon_v = 5$ eV, so that $\varepsilon_d - \varepsilon_f = 6.5$ eV. For U_{fd} a value of $\sim$2.5 eV seems reasonable as it is expected to be smaller than U_{ff} (cf [20]). This leads to $E(5f^2 6d(e_g)^1) - E(5f^3) \sim 3$ eV. This means that, under the assumptions made here, the 5f^3 states are lower in energy than the 5f^{2}6d(e$_g$)^1 ones and may therefore be related to the a and b structures. As these structures appear as shoulders on the low-energy side of peak c, their shapes and intensities are difficult to extract: what can be said is that they are spread over about 3.5 eV and that the two structures a and b are clearly visible. Such a width is in rather good agreement with bremsstrahlung isochromat spectroscopy (BIS [2]) that also gives access to the 5f^3 configurations. To account for this width one must consider the 5f electronic interactions, the spin–orbit coupling and the cubic crystal field. Indeed, for 5f compounds, the spin–orbit splitting is about 1 eV [24], which is of the same order of magnitude as the cubic crystal field. This leads to a very complex multiplet structure that may spread over several eV for the 5f^3 states. This contrasts with the case of CeO$_2$: in this compound one has to consider the 4f^1 final states: as there is only one f electron, as spin–orbit splitting is about 0.3 eV [24] and as the cubic crystal field can be neglected, the 4f^1 states are made up of a sharp peak. This is verified both by BIS [25] and by XAS oxygen K-edge experiments. The a and b structures in UO$_2$ therefore reflect the 5f^3 multiplet states hybridized with the O 2p ones. Their intensity is a fingerprint of the hybridization strength.

5. Conclusion

This interpretation of the O K-edge region has several consequences for the knowledge of the electronic structure of UO$_2$: firstly it constitutes direct experimental evidence of U 5f–O 2p hybridization in the ground state. Indeed, without such hybridization, no fingerprint of 5f^3 states would be detected in the spectrum. The U 5f–O 2p hybridization is smaller than the U 6d–O 2p hybridization for a number of empty states of the same order for the f and d states ($\sim$10 per uranium atom), the height of the a and b structures is smaller than for the c and d ones. However it is not negligible, which allows us to conclude that the U 5f–O 2p hybridization is not 'weak', and that calculations that would not take it explicitly into account would lead to unreliable results. Another important result is the nature of the insulating band gap. Following the definitions of [26], we have to compare the charge transfer energy $\Delta = 6.5$ eV [9], to the lowest cation–cation excitation energy: the latter may be either $U_1 = E(5f^2 6d^1) + E(5f^1 6d^0) - 2E(5f^2 6d^0) = \varepsilon_d - \varepsilon_f + 2U_{fd} - U_{ff}$ for a 5f–6d excitation, or $U_2 = E(5f^3 6d^0) + E(5f^1 6d^0) - 2E(5f^2 6d^0) = U_{ff} - J$ for an f–f excitation. With the values used above, we have $U_1 > U_2$ and $\Delta > U_2$, so that UO$_2$ can be classified

as a Mott–Hubbard insulator with an f–f gap, as suggested in [9], but in disagreement with [2, 3]. The fact that the O 2p states hybridized with the 5f ones are lower in energy than the O 2p states hybridized with the 6d ones, as results from our data, is an experimental confirmation of the f–f nature of the insulating gap, as it is well known that the top of the valence band is dominated by f electrons [2, 3]. The hypothesis of an f–d gap comes from the interpretation of the BIS spectrum: a small bump at the beginning of the BIS spectrum has been attributed to 6d electrons [2]. However, due to the high f electron cross-section in this energy range, the BIS spectrum is dominated by the contribution of the f electrons and it is very difficult to guess the contribution of the d electrons [6]. In contrast, at the oxygen K edge, only the hybridization strength modulates the contribution of the f and d electrons: as mentioned above, this allows us to clearly distinguish what structures come from the hybridization with the f and d electrons respectively, and the f electron contribution is found to be at the lowest energy.

Beyond the edge region (peaks a–d), the structures that appear on the XAS oxygen K-edge spectrum of UO_2 are attributed to oxygen 2p states hybridized with uranium 7s and 7p states. The extensive spread in energy for the oxygen 2p character is an indication of significant covalency. The high-energy features A to E have been identified as due to scattering from the shells of atoms located at average distances smaller than 4.74 Å from the oxygen emitter one in UO_2 following the same procedure as in [27]. A complete discussion of the XANES part of the O K x-ray absorption spectrum of UO_2 will be published in a forthcoming paper.

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