

Soft x-ray appearance potential spectroscopy study of NiO and CoO single crystal surfaces

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Soft x-ray appearance potential spectroscopy (SXAPS) spectra of Ni 2*p*, Co 2*p*, and O 1*s* for NiO and CoO single crystal surfaces have been measured. Two peaks and a shoulder along with two core lines due to 2*p*_{3/2} and 2*p*_{1/2} are found for a Ni 2*p* raw spectrum. A Ni 2*p* metallic edge was observed for the NiO surface sputtered by Ar ions. An O 1*s* spectrum of NiO exhibits a broad peak between about 522 and 550 eV and the self-deconvoluted spectrum shows five peaks. For the Co 2*p* spectrum, two core lines due to 2*p*_{3/2} and 2*p*_{1/2} along with a shoulder are found and the self-deconvoluted spectrum exhibits four peaks. The broad peak is also seen between about 525 and 555 eV for the O 1*s* spectrum of CoO and the self-deconvoluted spectrum shows four peaks. The features of the self-deconvoluted SXAPS spectra of Ni 2*p*, Co 2*p*, and O 1*s* for NiO and CoO are found to resemble those of the corresponding near edge x-ray absorption fine structure (NEXAFS). The origin of the peaks is discussed to compare the present work with the previous theoretical calculations for the NEXAFS spectra. © 2009 American Institute of Physics.

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I. INTRODUCTION

Appearance potential spectroscopy (APS), which can prove partial empty electronic states of surfaces, is a rather simple method to compare with x-ray absorption spectroscopy (XAS) usually using synchrotron radiation.¹ XAS is widely used for study of empty electronic states of materials because the excitation process is simple, follows the dipole selection rule, and the spectra are well theoretically studied.^{2,3} Nevertheless, APS has an advantage to be able simply to prove empty spin states of surfaces since a spin-polarized electron source can be applied to APS.⁴

Large incident electron currents (mA/cm²) were required to obtain good APS spectra because of small signal to background ratio, resulting in formation of surface damages on insulators. Although Auger electron APS can obtain the good spectra at low currents (10 μA/cm²),⁵ diffraction effects could be superimposed on APS signals especially for single crystal surfaces.⁶ We developed a high sensitive soft x-ray appearance potential spectrometer to solve the above problems.⁷

Since specific electron transitions in soft x-ray appearance potential spectroscopy (SXAPS) obey the “approximate dipole selection rule” (95%–80% of electron transitions from the specific core levels to empty states follow the dipole selection rule),⁸ the features of the SXAPS spectra are expected to resemble those of the near edge x-ray absorption fine structure (NEXAFS). However, only a few experimental SXAPS studies concerning the dipole selection rule have been reported on the 3*d* transition metal compounds.⁷

The SXAPS study was carried out on TiO₂ (110)–1 × 2 and (110)–1 × 1 surfaces.⁷ The self-deconvoluted SXAPS spectra were found to be similar to the NEXAFS.⁷ The

Ti 2*p*_{3/2} spectrum showed two strong peaks, which correspond to the transition to *t*_{2g} and *e*_g empty states. For the O 1*s* spectrum two strong peaks near the threshold were also found, which were ascribed to the transition to O 2*p*π and O 2*p*σ empty states. The result indicated that the spectra almost obey the dipole selection rule, so-called the approximate dipole selection rule. The spectra measured on the (110)–1 × 2 surface at an incident angle of 45° off normal to the surface and on the (110) surface sputtered by Ar ions showed that SXAPS is very sensitive to the surface electronic states.

The NEXAFS spectra of Ti 2*p* for TiO₂ were theoretically well explained by a single particle model because of a simple electronic transition from 2*p*⁶3*d*⁰ to 2*p*⁵3*d*¹. On the other hand the spectral line shape of the *L*-edge for late 3*d* transition metal oxides is complicated by several electronic factors, such as multiplet effects in the final states, spin and orbital polarizations, and spin-orbit coupling in both the initial and final states.^{2,3} As a result, many additional NEXAFS features were observed in the *L*-edge region, especially for oxides with partially filled *d*-orbitals.^{2,3}

We are interested in whether APS spectra of NiO and CoO with partially filled *d*-orbitals are similar to the corresponding NEXAFS ones or not because those of TiO₂ with a 3*d*⁰ configuration were found to be very similar to the NEXAFS. The samples were chosen for the present work since they were well studied by NEXAFS and various theoretical methods, leading to well understanding of the APS spectra by comparison with the NEXAFS spectra.

In this paper, we present the raw SXAPS spectra and their self-deconvoluted ones of Ni 2*p*, Co 2*p*, and O 1*s* for NiO and CoO single crystals. Since the theoretical calculation on the SXAPS spectra of the oxides has not been reported so far, the self-deconvoluted spectra are compared to the experimental and theoretical results on the 2*p* and 1*s*

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NEXAFS spectra for the oxides. The origin of the peaks in the self-deconvoluted SXAPS spectra is discussed.

II. EXPERIMENTAL

NiO (110) and CoO (100) single crystals were used in the present work. The crystal surfaces were cleaned by annealing at 550 °C in 1×10^{-4} Torr oxygen pressure because surface oxygen would be desorbed under an ultrahigh vacuum at high temperature. The cleanliness of the surfaces was confirmed by Auger electron spectroscopy. The CoO(100) surface showed (1×1) low-energy electron diffraction (LEED) patterns. On the other hand no LEED patterns were found for the NiO(110) surface.

A high sensitive SXAPS apparatus⁷ was used for the present work. The Ni 2*p* and Co 2*p* spectra were measured at an incident electron current, 50 $\mu\text{A}/\text{cm}^2$, and the measurements of the O 1*s* spectra for both the samples were carried out at 5 $\mu\text{A}/\text{cm}^2$. The LEED patterns for CoO were not changed after the measurements. All the raw spectra were obtained by 50 times acquisitions of the data. The detailed performance of the SXAPS apparatus and measurement conditions were described elsewhere.⁷

Since the APS spectral intensity is considered to be proportional to self-convoluted one-electron density of empty states,¹ the density of empty states for materials measured would be deduced by self-deconvolution of the APS spectrum. In the present work the self-deconvoluted spectra, expressed by a linear combination of the Gaussian functions and a straight background line, were obtained as follows: (1) a linear background was subtracted from the raw spectra and then the spectra were smoothed, (2) the spectra (the O 1*s* spectra in the present work) were differentiated to set the Gaussian peak position in the self-deconvoluted ones, (3) the spectra obtained in (1) was fitted by the self-convoluted spectra of the self-deconvoluted ones, and (4) this fitting procedure was continued until the *R* factor reaches as small a value as possible. The factor was between 9.88×10^{-4} and 1.48×10^{-4} .

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the raw and background subtracted SXAPS spectra of Ni 2*p* for NiO, respectively. The peaks at 846.4, 853.1, about 858.4 (broad), and 863.5, and a shoulder around 848 eV are found in Fig. 1(b). The peaks at 846.4 and 863.5 eV correspond to the transition from 2*p*_{3/2} and 2*p*_{1/2} core levels to the threshold of empty states, respectively, because the difference energy is 17.1 eV that is close to the Ni 2*p* spin-orbit splitting energy, 17.5 eV for NiO.⁹ The spectrum for the surface sputtered by Ar ions at 2 keV exhibited a pre-edge peak (not shown here) below the 2*p*_{3/2} edge by about 2.1 eV. This could be attributed to the transition from Ni 2*p*_{3/2} to the threshold of empty states for a Ni metal because the Ni 2*p*_{3/2} binding energy of the metal is lower by about 1.7 eV than that of NiO.⁹ This indicates that the surface is not reduced to the metal by electron bombardment during the measurement because of lack of the metal edge in Fig. 1. The threshold energy of Ni 2*p*_{3/2} for the present work is found to be 846.4 eV, which is lower by

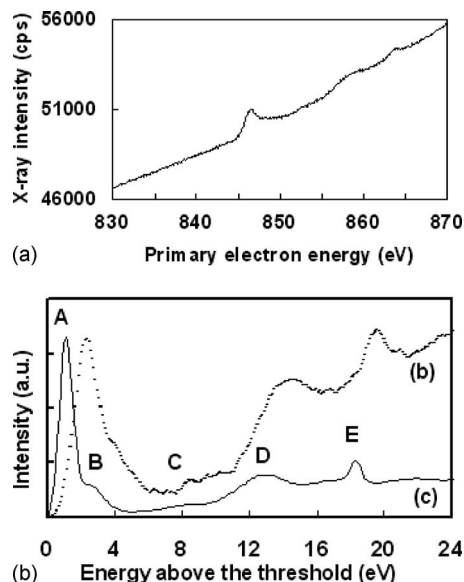


FIG. 1. (a) The SXAPS raw spectrum of Ni 2*p* for the NiO single crystal surface. (b) The background subtracted SXAPS spectrum of Ni 2*p* for the NiO single crystal surface. (c) The self-deconvoluted SXAPS spectrum of Ni 2*p* for the NiO single crystal surface.

about 8.7 eV (Ref. 9) than the binding energy obtained by x-ray photoelectron spectroscopy. This could be due to the charge-up and core-hole effects discussed in Ref. 7.

A self-deconvoluted spectrum of Ni 2*p* is displayed in Fig. 1(c), where five peaks (A–E) are seen. The Gaussian widths used in Fig. 1(c) are 0.9 (A), 2.0 (B), 2.0 (C), 2.9 (D), and 0.8 eV (E), respectively. Since the excitation process in APS is different from that in NEXAFS, the peak energy of the spectra obtained by both the methods cannot be directly compared. Therefore, we compare their relative peak energy in the present work. The relative peak energies to the first peak A are 1.7 (B), about 6.9 (C), 11.7 (D), and 17.0 (E) eV. The energy difference between peaks A and B almost coincides with the previous APS result although the APS spectrum was not measured above 6 eV from the threshold.¹⁰ A NEXAFS spectrum of Ni 2*p* for NiO showed the peaks at 1.9, about 6.4, 13.0, and 17.1 eV above the first strong peak,^{11–14} which is almost in agreement with our result in relative energy and intensity except the 13.0-eV peak.

Calculation of the multiplet structure of a $2p^5 3d^9$ final state configuration, taking into account of the atomic spin-orbit coupling, *p*-*d* and *d*-*d* Coulomb interactions, and crystal-field interaction, was performed using a cluster model.¹⁵ The result concluded that the five NEXAFS peaks could be attributed to transitions, $2p_{3/2} 3d^8 \rightarrow 2p_{3/2} 3d^9$ (the first and 1.9-eV peaks), $2p_{3/2} 3d^9 L \rightarrow 2p_{3/2} 3d^{10} L$ (the 6.4-eV peak), $2p_{3/2} 3d^9 L \rightarrow 2p_{3/2} 3d^9 Lk$ (the 13.0-eV peak), and $2p_{1/2} 3d^8 \rightarrow 2p_{1/2} 3d^9$ (the 17.1-eV peak), respectively,¹⁵ where $2p$, *L*, and *k* denote the 2*p* state with a hole, ligand hole, and continuum states, respectively.

The present result indicates that the self-deconvoluted SXAPS spectrum of Ni 2*p* for NiO is very similar in relative energy and intensity to the NEXAFS. Based on the analogy of an APS study on rare-earth compounds,¹⁶ since the APS excitation would be dominated by the resonant transition with both the incident and core electrons into empty states,

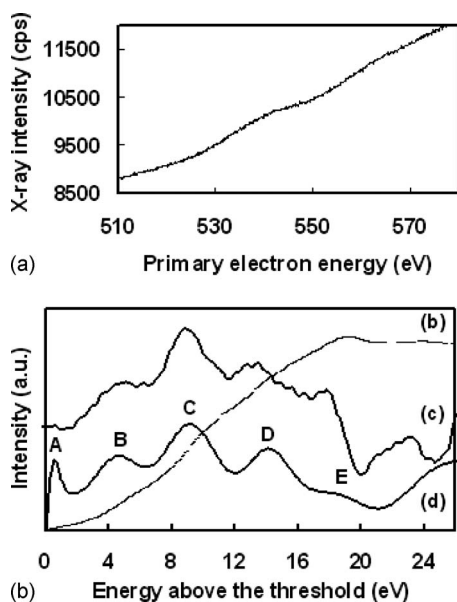


FIG. 2. (a) The SXAPS raw spectrum of O 1s for the NiO single crystal surface. (b) The background subtracted and smoothed SXAPS spectrum of O 1s for the NiO single crystal surface. (c) The derivative spectrum of (b). (d) The self-deconvoluted SXAPS spectrum of O 1s for the NiO single crystal surface.

the five peaks (A–E) would be attributed to the five transitions, $2p_{3/2}3d^8 + e \rightarrow 2p_{3/2}3d^{10}$ (A and B), $2p_{3/2}3d^9L + e \rightarrow 2p_{3/2}3d^{11}L$ (C), $2p_{3/2}3d^9L + e \rightarrow 2p_{3/2}3d^9Lk^2$ (D), and $2p_{1/2}3d^8 + e \rightarrow 2p_{1/2}3d^{10}$ (E), respectively. If peak D corresponds to the transition to the continuum states, it would be broad. The disagreement in the energy position of peak D with the 13.0-eV peak in the NEXAFS spectrum might be due to the fact that the self-convolution of broad density of states at high energy makes the peak position ambiguous or peak D might be due to the different processes discussed later.

Figures 2(a) and 2(b) show the raw, and background subtracted and smoothed SXAPS spectra of O 1s for NiO, respectively. A broad peak between about 522 and 550 eV is found in Fig. 2(b). A derivative spectrum is obtained in Fig. 2(c) to find out the peak position in Fig. 2(b). The peaks are found at 4.9, 9.0, 13.3, and 18.0 eV where the Gaussian peaks were first set. However, a peak at 0.5 eV was added to get good fitting since the fitting around the threshold was poor. The self-deconvoluted spectrum obtained thus is displayed in Fig. 2(d) where the five peaks [Gaussian width: A (0.8), B (3.3), C (4.3), D (3.3), and E (4.0 eV)] are found above the threshold. The relative peak energies to the first peak A are 4.2 (B), 8.6 (C), 13.7 (D), and 18.5 eV (E). This is almost in agreement with the relative energy for a previous second derivative O 1s APS spectrum for NiO:¹⁷ 4.8, 8.5, 13.3, and 16.7 eV although peak E is higher in energy than the previous result.

Many peaks were found between 530 and 570 eV for the O 1s NEXAFS spectrum of NiO.^{18–24} For example, the relative peak energies to the first peak a were 5.3 (peak b), 8.4 (peak c), 14.4 (peak d), and 24.0 eV (peak e).²⁴ To compare the present result with the NEXAFS spectra, the spectral features at low energy for the present work are similar to

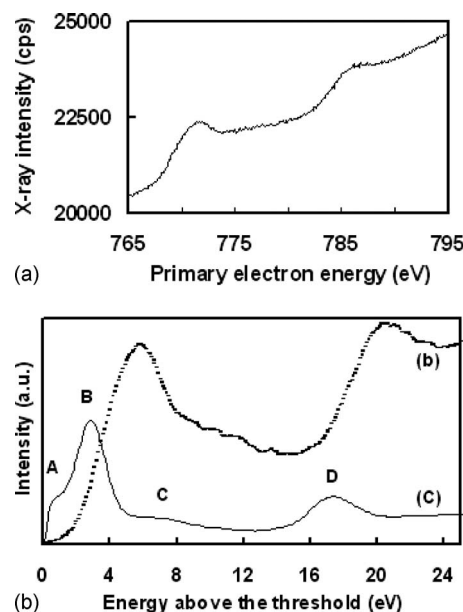


FIG. 3. (a) The SXAPS raw spectrum of Co 2p for the CoO single crystal surface. (b) The background subtracted SXAPS spectrum of Co 2p for the CoO single crystal surface. (c) The self-deconvoluted SXAPS spectrum of Co 2p for the CoO single crystal surface.

those of the O 1s NEXAFS spectrum in relative energy and intensity. However, the peak around 18.5 eV was not found in the NEXAFS spectrum.^{18–24}

First-principles molecular orbital calculations using a model cluster concluded that peaks a, b, c, and d could be attributed to the transitions to the empty O 2p states mixed with Ni 3d, 4s, and 4p states, respectively.²³ Although the result reproduced the major features of the O 1s near edge structures, it was pointed out that more quantitative agreement between theoretical and experimental results was required. The above explanation could be applied to the present SXAPS spectrum except for peak E, although the resonance transition also occurs in the O 1s excitation.

Figures 3(a) and 3(b) show the raw and background subtracted SXAPS spectra of Co 2p for CoO, respectively, where the peaks at 771.3, 777.3, and 786.4 eV are clearly seen in Fig. 3(b). Since the difference energy between the two strong peaks is 15.1 eV, the 771.3- and 786.4-eV peaks can be ascribed to the transitions from $2p_{3/2}$ and $2p_{1/2}$ to the threshold of empty states, respectively, because the Co 2p spin-orbit splitting energy for CoO is 15.2 eV.⁹ The threshold energy of Co $2p_{3/2}$ is found to be 767.3 eV that is also lower by about 13.0 eV than the binding energy,⁹ which could be explained by the same terms for the Ni 2p threshold discussed above.

The self-deconvoluted spectrum is displayed in Fig. 3(c) where four peaks [Gaussian width: A (0.6), B (2.1), C (3.1), and D (3.3 eV)] are found: The relative energies to the first peak A are 1.9 (B), 6.7 (C), and 16.8 eV (D). The five peaks with the relative peak energy position at 1.2, 1.7, 2.4, and 4.7 eV to the first peak was found for the Co 2p NEXAFS spectrum of CoO.^{25,26} The 1.2- and 1.7-eV peaks were not resolved in Refs. 27 and 28. Although the three peaks between 1.2 and 2.4 eV are not resolved in the present self-

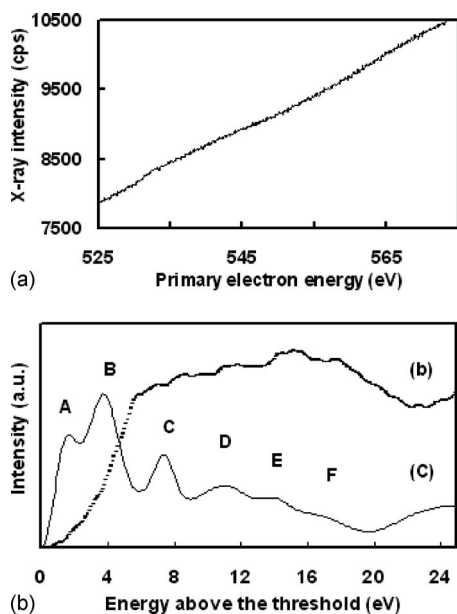


FIG. 4. (a) The SXAPS raw spectrum of O 1s for the CoO single crystal surface. (b) The background subtracted and smoothed SXAPS spectrum of O 1s for the CoO single crystal surface. (c) The self-deconvoluted SXAPS spectrum of O 1s for the CoO single crystal surface.

deconvoluted SXAPS spectrum, the spectral features of Co 2*p* resemble those of the NEXAFS spectrum except for the energy position of peak C.

Many theoretical calculations of electronic states and NEXAFS spectra for CoO were reported.^{25,29–36} The Co 2*p* NEXAFS spectrum was calculated using the atomic multiplet theory with inclusion of the cubic crystal field.³⁰ The calculation result for the transition from 3*d*⁷ to 2*p*⁵3*d*⁸ in the cubic crystal field (splitting energy: 0.9 eV) for Co²⁺ was in agreement with the NEXAFS spectrum. It was reported that the final states of the Co 2*p* NEXAFS spectrum were well understood in terms of atomic transition in the crystal field.²⁸ The main peaks around 779 eV were pointed out to be made up of the crystal-field split 2*p*⁵3*d*⁸ configuration, hybridized with the 2*p*⁵3*d*⁹*L* manifold,²⁸ where *L* denotes a ligand hole. The above result could be applied to the Co 2*p* SXAPS spectrum for CoO, although two electrons are allowed to be in empty 3*d* states.

Figures 4(a) and 4(b) show the raw, and background subtracted and smoothed SXAPS spectra of O 1s for CoO, respectively, where the broad peak is found between about 525 and 555 eV. The peaks were found at 4.4, 8.0, 10.7, 13.8, and 17.1 eV in the derivative spectrum (not shown here) of Fig. 4(b). A peak was also added at 1.5 eV to get good fitting. The self-deconvoluted spectrum is displayed in Fig. 4(c), where the five peaks [Gaussian width: A (1.4), B (2.0), C (1.5), D (2.9), E (1.9), and F (3.9 eV)] are found: The relative energies to the first peak A are 2.1 (B), 5.8 (C), 9.5 (D), 12.5 (E), and 15.6 eV (F). To compare the relative peak position of the present work with that of the NEXAFS spectrum of O 1s for CoO,²⁶ the peak positions are almost in agreement with the NEXAFS result at 1.7, 6.1, 9.1, 12.1 (very weak), and 14.9 eV above the first peak, although the peak intensity is different between them: The intensity of peaks D and C is weaker than that of B and A in the present work.

A cluster calculation²⁵ concluded that the two peaks near the threshold are due to the transition to Co 3*d* (with multiplet splitting) states mixed with O 2*p* states. It was also pointed out that the peaks above 535 eV could be ascribed to the Co 4*s* and 4*p* states mixed with O 2*p* and O 3*p* states. This suggests that peaks A and B correspond to the resonant transitions to Co 3*d* mixed with O 2*p* empty states, and peaks C, D, and F are due to the resonant transitions to the Co 4*s* and 4*p* states mixed with O 2*p* and O 3*p* states, respectively.

The above comparison of the present SXAPS result with the previous NEXAFS spectra indicates that the features of the self-deconvoluted 2*p* and O 1*s* SXAPS spectra for the late 3*d* transition metal oxides resemble those of the corresponding NEXAFS. This suggests that the approximate dipole selection rule is applicable to the 2*p* and 1*s* SXAPS spectra for the oxides (NiO and CoO). Although we have mainly considered x-ray emission through x-ray recombination process in APS,¹⁶ other processes such as decay from valence and core electrons into the core holes would contribute to the x-ray emission. However, such a contribution is less than the recombination process on the analogy of the previous result.¹⁶ Even if the core electrons are excited by nondipole process, x-ray emission through the decay of the excited electrons into the core holes cannot occur, resulting in no contribution to the SXAPS spectra.

The electron transmission in the APS process would significantly follow the dipole selection rule since most of the APS peaks coincide with those of NEXAFS in energy as found in the present work. However, some weak peaks at higher energy than the threshold are not seen in the NEXAFS spectra. This could occur when the core electrons are excited by nondipole process to empty states and valence or core electrons decay into the core holes by the dipole process, resulting in having weak peaks in the SXAPS spectra. This could be confirmed by energy analysis of emitted x-ray and the energy analysis would be necessary to study the APS process in detail. Some fine structures are not resolved in the SXAPS spectra, presumably due to self-convolution.

IV. SUMMARY

The SXAPS spectra of Ni 2*p*, Co 2*p*, and O 1*s* for the NiO and CoO single crystal surfaces were measured. The five peaks (A–E) are found for the self-deconvoluted Ni 2*p* spectrum of NiO: the relative energies to peak A are 1.7 (B), about 6.9 (C), 11.7 (D), and 17.0 eV (E). The Ni 2*p* metallic edge below the threshold by about 2.1 eV was found for the NiO surface sputtered by Ar ions. This indicates that SXAPS is very sensitive to the surface electronic states. The self-deconvoluted spectrum of O 1*s* for NiO shows the five peaks (A–E) with the relative energy to the first peak A at 4.2 (B), 8.6 (C), 13.7 (D), and 18.5 eV (E). The Co 2*p* self-deconvoluted spectrum exhibits the four peaks (A–D) with the relative energy to peak A at 1.9 (B), 6.7 (C), and 16.8 eV (D). For the O 1*s* self-deconvoluted spectrum of CoO the five peaks (peaks A–E) are found: The relative peak energies to peak A are 2.1 (B), 5.8 (C), 9.5 (D), 12.5 (E), and 15.6 eV (F). The comparison of the present SXAPS result with the

previous NEXAFS spectra indicates that the features of the self-deconvoluted $2p$ and $O\ 1s$ SXAPS spectra for the late $3d$ transition metal oxides resemble those of the corresponding NEXAFS. Some fine structures are not resolved in the SXAPS spectra, presumably due to self-convolution. The origin of the peaks is discussed to compare with the previous theoretical calculations for the NEXAFS spectra.

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