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Ultrathin alumina film on Cu-9at%Al(111)

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ABSTRACT

We have investigated the structure of the clean and the oxidized (111) surface of a Cu-Al alloy with 9 at% Al by scanning tunneling microscopy (STM), Auger electron spectroscopy (AES), low energy ion scattering (LEIS) and low energy electron diffraction (LEED). Annealing of the clean crystal at 680 °C leads to segregation of Al to the surface. The Al concentration at the annealed surface is $23 \pm 2\%$ and domains with a $(\sqrt{3} \times \sqrt{3})$ R30° superstructure are visible, as well as small Cu(111) areas and disordered patches. Oxidation at 680 °C leads to the formation of a well-ordered flat alumina film with two very similar oxide structures. One oxide structure has a nearly commensurate rectangular cell rotated by 30° with respect to a close-packed row of the substrate and grows in three different domains. The second structure has a commensurate cell consisting of four equivalent building blocks and has a rectangular centered symmetry. This structure is rotated by 18° with respect to a close-packed row of the substrate and grows in six different domains. The rectangular building blocks of these two oxide structures have a similar thickness, the same surface termination and the same number and arrangement of the atoms as the oxide film on NiAl(110) [G. Kresse, M. Schmid, E. Napetschnig, M. Shishkin, L. Köhler, P. Varga, Science 308 (2005) 1448]. In contrast to the oxide on NiAl(110), alumina on the Cu-Al alloy crystal does not show stress-induced domain boundaries and grows in large defect-free domains. Thus, Pd deposited on this oxide nucleates not only on domain boundaries and steps but also on the unperturbed oxide, forming (111)-oriented clusters.

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1. Introduction

Thin alumina films grown on various metal substrates are of interest for different technological applications. They are used in catalysis, for gas sensors, as coatings and in microelectronics. In research, a very common application is the use of thin alumina films on a metal substrate as a support for metal particles serving as model catalysts. Using such ultra thin oxide films eliminates charging problems when applying measurement methods involving charged particles. For well-defined and reproducible results, the alumina film has to be well ordered. Since more than two decades, many groups have attempted to find suitable substrates and recipes for growing such ultra-thin alumina films [1–7].

The Cu–Al(111) alloy with 9 at% of Al is one of the substrates where growth of a well ordered Al_2O_3 film was reported [8–10]. Concerning the clean (not oxidized) alloy, Auger electron spectroscopy (AES) measurements show an increase of the Al concentration at the surface when the crystal is annealed in ultrahigh vacuum (UHV) [11,12]. The different Al concentrations at the surface induce different superstructures, which are visible in low-energy electron diffraction (LEED) [11,12]. At low annealing temperatures the LEED pattern indicates a (1×1) structure which evolves to a diffuse $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ pattern at elevated temperatures. While the sample is at high temperatures, LEED shows a (1×1) pattern again. The temperature reported for the second reversible transition is between 227 °C [13] and 327 °C [11].

The high Al concentration at the surface, reported as 22% Al at the surface [12], should make it possible to grow a stoichiometric alumina layer. It was argued that the relatively small misfit of 6-8% between the close-packed O planes of α -Al₂O₃ or γ -Al₂O₃ and the Cu–9at%Al(111) lattice should facilitate epitaxial growth [8]. Recent studies [8-11] have reported the formation of 0.4-3.5 nm thick γ -Al₂O₃-like alumina films with a $(7/\sqrt{3} \times 7/\sqrt{3})R30^{\circ}$ structure on Cu-9at%Al(111) after oxygen adsorption at temperatures between 577 and 725 °C, using rather high O2 doses (1200-4000 L; 1 L = 1.33×10^{-6} mbar s). In these studies, AES, XPS (X-ray photoelectron spectroscopy), SEM (scanning electron microscopy), LEED and RHEED (reflection high energy electron diffraction) were used. As STM (scanning tunneling microscopy) measurements were missing for the clean surface as well as for the alumina-covered crystal, in our work we have focused on STM measurements.

We compare our findings on the alumina film grown on Cu– 9at%Al(111) with the well-known thin alumina film on NiAl(110).





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For the alumina film on NiAl(110), the oxide film structure was determined recently by combining STM images and density functional theory calculations [14]. The alumina film on NiAl(110) has a structure and a stoichiometry that differs from all Al₂O₃ bulk phases. It has a nearly rectangular unit cell (a = 18.0 Å, b = 10.6 Å; bold lines in Fig. 1) in two reflection domains. The unit cell has twofold rotational symmetry with glide planes parallel to the two sides of the unit cell, i.e., *p2gg* plane-group symmetry. The film consists of two aluminium and two oxygen layers and the surface is oxygen terminated. Fig. 1a shows the two topmost layers, named O_s and Al_s ("s" for surface). Both layers have been imaged by STM, O_s at room temperature and Al_s at low temperatures [14]. The O_s layer shows triangular and square atomic arrangements and con-

sists of 28 atoms per unit cell. The Al_s layer is only 0.4 Å lower than the topmost layer and has 24 atoms per unit cell, which are all in the center of either a triangle or a square of the O_s atoms. The Al_s layer has a slightly distorted hexagonal structure. The O atoms of the third alumina layer, named O_i ("i" for "interface"), replicate the Al_s lattice; each O_i atom is located below an Al_s atom [14]. Fig. 1b shows the atomic structure of this layer together with the atomic positions of the interfacial Al_i layer. The 16 Al_i atoms are arranged in pentagon-heptagon pairs and can be probed by STM at larger tip sample distances [14]. The Al_i atoms are located preferentially above Ni rows of the substrate and avoid its Al rows. This row matching leads to a compressive stress and a slight distortion of the rectangular oxide cell.



Fig. 1. The atomic arrangement of the alumina film on NiAl(110). (a) The surface – a square and triangular arrangement of oxygen atoms is marked, and the thin lines mark rows of Al_s atoms leading to a strong (6,2) LEED spot. (b) The third (oxygen) and fourth (aluminium) layer. Ni rows of the underlying NiAl(110) surface are indicated by vertical lines.

The alumina film on NiAl(110) exhibits two types of domain boundaries [15–17], reflection domain boundaries between different orientations of the oxide and line defects separating areas of the same orientation of the oxide. The latter are often referred to as anti-phase domain boundaries and caused by the stress due to row matching with the substrate [17]. The domain boundaries appear bright in STM images at higher positive bias voltages because of unoccupied states localized at the domain boundaries [17,18]. Both, antiphase and reflection domain boundaries can act as nucleation centers for metal clusters on the alumina film on NiAl(110) [7]. For example, Pd clusters nucleate at defects on the alumina surface, i.e., at domain boundaries and step edges [19,20].

2. Experimental

The Cu–9at%Al(111) sample was prepared by 2 keV Ar⁺ sputtering and annealing at 680 °C for 10 min in a UHV chamber with a base pressure in the low 10^{-10} mbar range. The temperature was measured by a thermocouple, which was mounted on the nontransferable part of the sample holder and thus showed a different temperature (600 °C). The true sample temperature was determined with a disappearing filament pyrometer, calibrated with the thermocouple to eliminate the influence of light attenuation by the viewport. We have checked the cleanness of the sample after sputtering and annealing with AES. After several cycles of sputtering and annealing, no impurities like sulphur or carbon were detected. Unless noted otherwise, the alumina film was prepared by dosing of 100 L oxygen with an oxygen partial pressure of 1.3×10^{-7} mbar at 680 °C. STM, AES, LEED and low-energy ion scattering (LEIS) measurements were performed at room temperature in the analysis chamber, which has a base pressure below 5×10^{-11} mbar. The STM measurements were performed using a customized commercial STM (Omicron µ-STM) with an electrochemically etched W tip. All STM images were obtained in constant current mode. LEIS measurements were carried out with 1 keV He⁺ ions at a scattering angle of 90° and a current density of about 3 nA/mm². The LEIS spectra were obtained with a hemispherical energy analyzer operated with fixed retardation ratio. AES spectra were taken with a cylindrical mirror analyzer (CMA) with a concentric electron gun and 3 keV electron energy; the Auger peakto-peak heights (APPH) of the differentiated spectra were used for quantitative analysis. Pd was deposited from a rod using a water-cooled electron-beam evaporator (Focus EFM3). During deposition a retarding voltage was applied to the orifice of the evaporator to suppress high-energy metal ions from the evaporator, as such ions otherwise create nucleation centers on the surface [21]. The deposition rate, calibrated with a quartz crystal microbalance, was 0.07 ML/min. We define 1 ML Pd here as the amount of atoms in one Pd(111) layer.

3. Results

3.1. Pure Cu-9%Al(111) crystal

We have investigated the clean Cu–9%Al(111) surface after annealing at 680 °C, the same temperature as used for oxidation. The LEED image shows a diffuse ($\sqrt{3} \times \sqrt{3}$)R30° pattern (Fig. 2a). Since cooling in our system is not fast enough to freeze the hightemperature (1 × 1) phase, this observation is in agreement with Refs. [11,13]. We have obtained atomically resolved STM images with chemical contrast (Fig. 2b and c). Since the atomic radius of Al is larger than that of Cu, and Al is the more reactive metal, we attribute the bright species to Al, in agreement with the surface composition known from the literature [12] (see below). The images show areas with a ($\sqrt{3} \times \sqrt{3}$)R30° superstructure (marked "A" in Fig. 2b) as well as areas of pure Cu(111) (marked "B"), mainly at the domain boundaries of the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ structure. Additionally, there are also a few small areas (marked "C") where the Al atoms are locally denser than in the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ structure.

We have drawn the (1×1) lattice over the atomically resolved STM images with chemical contrast (Fig 2c) and measured the heights on the (1×1) positions, resulting in a bimodal distribution (Fig. 2d). The histogram can be fitted by a superposition of two Gaussian distributions. The ratio of the concentrations of Cu and Al in the surface is equal to ratio of the areas under the two Gaussians. The quantification results in a surface concentration of $23 \pm 2\%$ Al, in excellent agreement with the previous AES result of 22% obtained after annealing at a somewhat lower temperature [12].

3.2. Oxidized Cu-9%Al(111) crystal

After sufficient cleaning, oxidation of the crystal at 680 °C led to a surface covered by a well-ordered flat oxide film with large domains and thus very good long range ordering (Fig. 3). To estimate the thickness and surface composition of this oxide film we compared it with the alumina film on NiAl(110), which has a wellknown thickness, stoichiometry and surface composition [14,15]. For the estimation of the thickness we calculated the expected AES spectrum with the AES database SESSA [22] for the two crystals covered by a thin alumina film. The results were corrected by assuming that the sensitivity of the CMA is proportional to the energy. Considering that we do not know the exact energydependent analyzer sensitivity, that we use Auger peak-to-peak heights instead of intensities and also considering possible systematic errors of the electron transport calculation, we should not directly compare the experimental and calculated results. Nevertheless, assuming that the oxide films on both substrates are equal, and further assuming equal influence of instrumental factors on the Ni (848 eV) and Cu (920 eV) substrate lines, the experimental intensity ratio between the oxygen line (510 eV) and the substrate lines should be proportional to the calculated one. Table 1 shows that the proportionality factor between measured and calculated oxygen/substrate ratios is only 6% lower for the oxide on Cu-9at%Al(111) than for the oxide on NiAl(110). This deviation is within the experimental uncertainty as well as within the uncertainty of the calculation (both are estimated around 10%). These results allow us to rule out a significantly different thickness of the oxide, especially a different number of layers: removing the interfacial layers Ali and Oi would result in a calculated O/Cu intensity ratio of 0.29; duplicating these layers gives a ratio of 0.92.

To determine the composition of the uppermost layer of the oxide film on Cu–9%Al(111), we compared the ratios of the areas of the oxygen to the Al peak in the LEIS spectra of the oxide films on the two substrates. For the oxide on Cu–9%Al(111), the O/Al peak intensity ratio was 0.72, which is 6% below that of the oxide on NiAl(110). Considering the experimental error, this points to a similar or possibly the same surface composition of the oxides on Cu–9%Al(111) and NiAl(110).

The LEED pattern of the oxidized surface of the Cu–9%Al(111) crystal is shown in Fig. 4. It is a complex pattern with a multitude of reflections, different from the diffraction pattern reported in Refs. [8,10,11,13]. The LEED pattern shown is slightly distorted due to residual magnetic fields and a non-perfect geometry. Nevertheless, we can use the pattern to derive the unit cells, a procedure aided by the STM images (see below). The first structure (Fig. 4a) is a rectangular one with three rotational domains, nearly commensurate with the substrate. The unit cell dimensions, derived from the LEED pattern, are 18.2 Å \times 10.6 Å. The long side of the unit cell is rotated by 30° with respect to a close-packed row of the sub-



Fig. 2. The clean Cu–9%Al(111) crystal after annealing at 680 °C. (a) LEED pattern taken at 90 eV with the reciprocal cell of the $(\sqrt{3} \times \sqrt{3})$ R30° superstructure marked. (b) Atomically resolved STM image (100 Å × 80 Å; 2 mV/10.5 nA) with chemical contrast (Al atoms appear bright and Cu atoms dark) showing areas with an Al $(\sqrt{3} \times \sqrt{3})$ R30° superstructure (A), pure Cu(111) areas (B) and Al-rich defects (C). A domain boundary (DB) of the Al $(\sqrt{3} \times \sqrt{3})$ R30° superstructure is marked. (c) Atomically resolved STM image (100 Å × 100 Å; 1 mV/39.2 nA) with the (1 × 1) lattice marked by white points. (d) Histogram of the heights at the lattice positions (grey). The black line is a fit by a sum of two Gaussian distributions.



Fig. 3. STM image of the oxidized surface (3000 Å \times 3000 Å; 2.8 V/0.4 nA). Domain boundaries in the oxide are visible as bright lines.

strate. Also the second oxide structure has a rectangular cell (Fig. 4b), with a size of $18.3 \text{ Å} \times 10.6 \text{ Å}$, rotated by $\pm 18^{\circ}$ with respect to a close-packed row of the substrate and therefore forming six rotational domains. Two by two of these rectangular building blocks form a larger commensurate cell with centered symmetry. Both superstructures show weak or no intensity of the odd LEED spots on the axes (squares in Fig. 4; the intensity visible in some squares can be attributed to different spots of another domain). This indicates p2gg symmetry of the rectangular cells, which is the plane group of the surface oxide on NiAl(110). Both superstructures on Cu-9%Al(111) show strong (6,2) or (6,-2) spots. These are also strong spots for the LEED pattern of the surface oxide on NiAl(110) (see, e.g., Fig. 10 of Ref. [7]). Considering that Al is a stronger scatterer for electrons than oxygen, these spots are mainly caused by the Al_s rows marked in Fig. 1a. The other superstructure spots, even if they are strong at one electron energy, get weaker at most other energies (e.g., the (3,1) or (3,-1) spots, which are quite strong in Fig. 4).

Atomically resolved STM images taken at very low tunneling voltages in the mV range show that the unit cell of the first oxide structure (Fig. 5a) and one building block of the second structure (Fig. 5b) have the same amount of atoms and an identical arrangement of the atoms. The 28 visible atoms are arranged in squares and triangles with p2gg symmetry. Not only the number of atoms and the symmetry but also the atomic structure are the same as for the surface oxygen (O_s) layer of the ultrathin alumina film on

Table 1	
Measured and calculated [22] Auger intensity rations for the alumina films on Cu–9%Al(111) and NiAl(110)

Substrate	Auger lines (eV)	Experimental APPH ratio	Calculated intensity ratio	Ratio experimental/calculated
Cu-9%Al(111)	O(510)/Cu(920)	0.75	0.60	1.25
NiAl(110)	O(510)/Ni(848)	1.29	0.97	1.33

Calculated intensities are corrected for the transmission of the analyzer, which is assumed to be proportional to the energy. For both substrates, calculated ratios assume the film composition, density and thickness determined for NiAl(110).

NiAl(110) [14] imaged by STM at similar tunneling conditions (Fig. 5c).

Fig. 5d–f shows STM images taken at larger tip sample distances, where we know from the studies of the oxide on NiAl(110) that the Al_i layer is imaged [14,17]. Although we have not obtained images of comparable quality as for NiAl(110) (Fig. 5f) of this layer, the STM images (Fig. 5d and e) indicate that both structures on Cu–



Fig. 4. LEED pattern of the oxidized surface taken at 90 eV. The reciprocal lattices of the rectangular oxide structures marked are rotated by (a) 30° and (b) 18° with respect to the close-packed directions of the substrate. In the right side symmetry-equivalent rotational domains are also indicated. The integer-order maxima of the substrate are circled in (a), and small squares show positions with vanishing intensity in a structure with *p*2gg symmetry and one domain.

9%Al(111) show 16 atoms, arranged in heptagon and pentagon pairs exactly as for the Al_i of the alumina film on NiAl(110).

Coming back to the large-scale images of the oxide film on the Cu–Al alloy crystal taken at positive bias voltage (e.g., Fig. 3), we can now determine that the bright lines are rotational domain boundaries in the wider sense, i.e., boundaries between two different rotations of essentially the same kind of structure. Having understood the structure, we have to expect three domains of the non-commensurate structure shown in Figs. 4a and 5a (three rotations of the rectangle; no mirror domains because of the *p2gg* symmetry) and six domains of the commensurate structure shown in Figs. 4b and 5b. Domain boundaries can occur between any of these nine domains. In our STM images, we did not observe any lines caused by antiphase (translational) domain boundaries like those forming the majority of the line defects in the oxide film on NiAl(110) [15–18].

We finally note that the ultrathin oxide described here is not the same oxide structure as observed by Yoshitake et al. [8– 11,13]. Using a slightly lower pressure and temperature (6.5×10^{-8} mbar, approx. 580 °C), but a significantly higher oxygen dose (1000 L) than for preparation of the ultrathin films described above, we have obtained a LEED pattern dominated by the ($7/\sqrt{3} \times 7/\sqrt{3}$)R30° structure reported in these papers, but with an additional weaker contribution of the 30°-rotated structure described above. AES showed an O/Cu ratio twice as high as for the ultrathin oxide described above, indicating a thicker oxide.

3.3. Palladium clusters on the alumina film

Fig. 6a shows an STM image after deposition of 1 ML Pd at room temperature. The cluster density of the Pd clusters on the alumina film on the Cu–Al alloy is $0.18\times 10^{16}\ clusters/m^2$, about 1/6th of the density on the alumina film on NiAl(110). The clusters on alumina/Cu-9%Al(111) are larger, however, with typical side lengths between 10 and 20 nm, in contrast to 5-10 nm on the oxidized NiAl(110) crystal. On both oxides, the Pd clusters have a truncated triangular shape with flat facets on top, indicating (111) orientation [19,20]. In contrast to the film on NiAl(110), there are very few high Pd clusters with a steep slope and a round top. Fig. 6b shows the height distribution of the Pd clusters. It has distinct maxima that are separated by the Pd(111) interlayer distance, confirming the (111) orientation of the clusters. The heights given in this histogram are the values measured from the STM image, uncorrected for the voltage dependent apparent thickness of the oxide film (discussed in Ref. [20]). We estimate that the true cluster height is about 2 Å lower, thus the maximum of the true height distribution is at 18 Å, only one or two layers higher than on the oxide on NiAl(110).

The nucleation sites are different from the ones on the oxide of NiAl(110). Apart from Pd clusters nucleating on the domain boundaries and the step edges there are also Pd clusters at positions where no domain boundaries are visible.

4. Discussion

Our STM results show that the alumina film on the Cu– 9%Al(111) crystal has exactly the same surface structure as the



Fig. 5. STM images of (a-c) the surface oxygen layer with atomic resolution and (d-f) the interface Al layer visible at somewhat higher tunneling resistance. The left images (a,d) show the first (incommensurate) oxide structure and the center images (b,e) show the second (commensurate) oxide on Cu-9%Al(111). The oxide on NiAl(110) is shown for comparison (right). In all images, the dots mark the atomic positions of the respective layers calculated for alumina on NiAl(110) [14]. In (b,e) the primitive unit cell is drawn in black and the four rectangular building blocks are marked in white.



Fig. 6. (a) STM image $(2500 \times 2500 \text{ Å}^2, 2.8 \text{ V}/0.2 \text{ nA})$ (b) and cluster height distribution after deposition of 1 ML Pd on the alumina film on Cu–9%Al(111) at room temperature.

film on NiAl(110) [14]. As this structure is unique among all alumina structures found so far, we conclude that also the thickness and composition of the oxide is the same as on NiAl(110), and our STM images also indicate the same structure at the interface. Also our AES and LEIS values indicate essentially the same thickness and composition of the ultrathin oxides on the two substrates and rule out any significant differences such as a different number of layers. An even more sensitive indicator of the oxide composition is the appearance in STM images at positive voltages near the conduction band edge, where deviations from the charge–neutral stoichiometry lead to band bending, which is easily detected by STM [17]. With the exception of the domain boundaries, we did not find any indications for such deviations from charge neutrality. As the oxides on Cu–9%Al(111) and NiAl(110) have the same structure, we must conclude that this structure, with its tight intertwining of oxygen triangles and squares at the surface is highly favorable, also in absence of the interfacial constraint imposed by the row matching on the NiAl(110) surface. This notion is supported by our experience that the preparation of the ultrathin alumina film on Ni₃Al(111), which is structurally similar, but with the O_s triangles and squares in more separate areas [23], has a much narrower window of preparation parameters than the oxides on NiAl(110) and Cu–9%Al(111), indicating a lower stability of the oxide on Ni₃Al(111).

The main differences between the oxide films on Cu-9%Al(111)and NiAl(110) are the slightly different unit cell dimensions. Compared to the slightly sheared rectangle on NiAl(110), the lattice of the oxide structures on the Cu-Al alloy crystal is rectangular and expanded by 1-2% in the direction of the longer side of the unit cell. This can be explained by the row matching between the oxide and the NiAl(110) substrate, which exerts compressive stress on the oxide along one diagonal of the rectangular cell [17]. On Cu-9%Al(111), one of the unit cells is incommensurate with the substrate in all directions, thus it can freely assume its preferred lattice dimensions. This tells us that the potential energy surface of the Cu-9%Al(111) substrate is less corrugated than on NiAl(110). This fact may be explained on the one hand by the much weaker tendency towards chemical ordering in Cu-Al alloys compared to NiAl, making it possible to avoid the unfavorable configuration [14] of having a substrate Al atom below an Al, atom of the substrate. On the other hand the energy gain of a heteroatomic Al-Cu bond between oxide and substrate is much lower than for an Al-Ni bond, as indicated by enthalpies of alloy formation [24]. The absence of row matching and, thus, compressive stress in the oxide on Cu-9%Al(111) is also the reason why there are no antiphase domain boundaries in this film, leading to larger areas free of domain boundaries.

The lower density of domain boundaries leads to a lower density of Pd clusters nucleating on Cu–9%Al(111). On alumina/ NiAl(110), Pd clusters nucleate exclusively on domain boundaries, while the distance between the domain boundaries on Cu-9%Al(111) is so large that Pd clusters nucleate also between them. We cannot determine whether Pd nucleation between the domain boundaries is homogeneous nucleation or induced by point defects, but STM images of the pure oxide show no indication of such defects. The orientation and overall shape of the Pd clusters is the same on both oxides, but the clusters on alumina/Cu-9at%Al(111) are about two times as large in their in-plane dimensions, though only 1–2 ML (\approx 10–20%) higher . This provides another confirmation of our previous conclusion [20] that the height/width ratio is not determined by energy minimization but rather by kinetic limitations of interlayer mass transport.

5. Conclusions

When a clean Cu-9at%Al(111) crystal is exposed to oxygen at 680 °C, a well ordered flat thin alumina film grows, which has the same structure and properties as the alumina film on NiAl(110), except for the absence of compressive stress and the antiphase domain boundaries caused by the stress. Thus, the oxide film on Cu-9%Al(111) grows in large, probably defect-free domains. The only defects visible by STM are the domain boundaries between the nine different orientations of the alumina structure on the substrate. We can conclude that the oxide structure found on NiAl(110) seems to be the most stable structure for a thin alumina film on different substrates and that Cu-9%Al(111) is an ideal substrate to grow an alumina film with a very good long-range ordering. A different density of domain boundaries on Cu-9%Al(111) and NiAl(110) makes it possible to obtain different metal cluster densities on the same oxide, which is interesting for studies of model catalysts.

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