Ordinary dielectric function of corundumlike α -Ga₂O₃ from 40 meV to 20 eV

Martin Feneberg* and Jakob Nixdorf

Institut für Experimentelle Physik, Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany

Maciej D. Neumann and Norbert Esser

Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Schwarzschildstrasse 8, 12489 Berlin, Germany

Lluís Artús and Ramon Cuscó

Institut Jaume Almera (ICTJA-CSIC), Consejo Superior de Investigaciones Científicas, 08028 Barcelona, Spain

Tomohiro Yamaguchi

Department of Electrical Engineering and Electronics, Graduate School of Engineering, Kogakuin University, 2665-1 Nakano, Hachioji, Tokyo 192-0015, Japan

Rüdiger Goldhahn

Institut für Experimentelle Physik, Otto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany

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The linear optical response of metastable α -Ga₂O₃ is investigated by spectroscopic ellipsometry. We determine the ordinary dielectric function from lattice vibrations up to the vacuum ultraviolet spectral range at room temperature for a sample with a (0001) surface. Three out of four E_u infrared-active phonon modes are unambiguously determined, and their frequencies are in good agreement with density functional theory calculations. The dispersion of the refractive index in the visible and ultraviolet part of the spectrum is determined. High-energy interband transitions are characterized up to 20 eV. By comparison with the optical response of α -Al₂O₃ and with theoretical results, a tentative assignment of interband transitions is proposed.

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I. INTRODUCTION

The wide-band-gap semiconductor gallium oxide has a multitude of potential applications in spintronics [1], sensorics [2], solar-blind detectors [3], and transparent electronics [4,5]. It has long been known that Ga₂O₃ crystallizes in several different polytypes [6], each with distinct physical properties. The thermodynamically stable phase is the monoclinic β phase which shows great potential for use as substrate material because it can be synthesized in thick boules [4,7–9]. Due to its high chemical and thermal stability matched with a large band gap and high breakdown voltage, this polytype has received increasing attention during the last decade. Specifically, the optical properties of monoclinic β -Ga₂O₃ were investigated in detail. Because of low crystal symmetry, phonon contributions [10,11] and interband transitions [11–13] are described by dielectric tensors containing four different nonzero tensor components. The Raman selection rules and tensor components are strongly influenced by the anisotropic properties of the material [14,15].

Additionally, other metastable polytypes of Ga₂O₃ are known, and their precise physical properties and even their crystal structures are still partly under debate [16,17]. These polytypes have not been studied yet in sufficient detail to

unleash their obviously high potential. The corundumlike α phase of Ga₂O₃ [18] is especially attractive for technological and scientific purposes. Its most prominent advantage is the seamless integration with α -Al₂O₃, which is available as high-quality large-area substrates at a relatively low price [19–21]. Moreover, several metal oxides that crystallize in the corundumlike structure are also available as bulk, e.g., Cr₂O₃ [22], opening the opportunity to investigate alternative substrates for α -Ga₂O₃. The possibility to create alloys [23] with α -In₂O₃ [24–28] or α -Al₂O₃ is a further invaluable advantage. Consequently, the growth of phase pure alloys [29] and advanced functional heterostructures is possible [30].

α -Cr₂O₃ is known for its interesting magnetic properties [22,31–33], and, similarly to Fe₂O₃, V₂O₃, or Rh₂O₃ in their corundum form, this magnetic oxide is nearly lattice matched to α -Ga₂O₃ [34,35]. Alloys of these materials with α -Ga₂O₃ [36] can be developed to realize new functionalities exploiting the semiconducting properties of α -Ga₂O₃ [37,38] in conjunction with magnetic properties of corundumlike rare-earth oxides.

Experimental studies of the optical properties of α -Ga₂O₃ are rather scarce. Phonon modes were investigated by Raman spectroscopy [39]. Electrical, optical, and magnetic properties of doped material were also studied [40]. Recently, we reported the properties of the fundamental absorption edge at 5.61 eV [41]. Some studies investigated α -Ga₂O₃ by means of first-principles computations [17,42–44].

*martin.feneberg@ovgu.de

Here, we provide ellipsometry data for photon energies spanning the range from infrared lattice vibrations up to interband transitions of α -Ga₂O₃. We employ state-of-the-art spectroscopic ellipsometry experiments spanning an unusually large photon energy range [from ~ 40 meV (330 cm^{-1}) up to 20 eV] to obtain the dielectric function of the material. We compare the result with previous first-principles calculations and with ellipsometry results obtained on α -Al₂O₃. The optic axis of the sample used in this study was normal to the sample surface. Therefore, in normal-incidence experiments the electric field vector ($\vec{E}$) is perpendicular ($\perp$) to this axis (c or [0001] direction) and consequently, only the ordinary component of the dielectric tensor is accessible [41].

Spectroscopic ellipsometry is considered to be an extremely sensitive tool to determine the linear optical response of materials. It can be easily implemented to work with uniaxial materials [45] (like corundum) and is sensitive to small anisotropies [46,47]. For our sample geometry, in which an oblique angle of incidence was used, only the ordinary dielectric function can be accessed with high sensitivity. The influence of the extraordinary tensor component can be modeled empirically in the infrared spectral region [48]. In the transparency regime, the effects of the extraordinary tensor element are negligible [49]. Only slight deviations of amplitudes may occur when describing interband transitions [50], while energy positions are correctly reproduced in the geometry used [51]. The influence of sample anisotropy becomes visible only in the case of materials where the extraordinary imaginary part of the dielectric tensor component yields a strong contribution while the ordinary one is close to zero. This occurs around the band edge of wurtzite AlN [52]. However, this is not the case for corundumlike α -Ga₂O₃, in which normal-incidence transmission and spectroscopic ellipsometry measurements yield similar absorption line shapes [41].

II. EXPERIMENTAL DETAILS

An α -Ga₂O₃ thin film grown by ultrasonic mist chemical vapor epitaxy on (0001) α -Al₂O₃ substrate was investigated experimentally. The substrate temperature was kept constant at 200 °C during the growth. The layer thickness was 473 nm, the root-mean-square surface roughness as measured by atomic force microscopy was 4.4 nm on a $1 \times 1\text{ }\mu\text{m}$ scan area [53]. High-resolution x-ray diffraction of the sample provides an out-of-plane lattice parameter of 13.418 Å close to reported values [53,54]; therefore the layer is considered to be nearly or fully relaxed. The FWHM of a symmetric ω scan of the (0006) reflex yielded 85 arcsec [53]. The sample was investigated by spectroscopic ellipsometry using different instruments in the different spectral ranges. In the infrared spectral range ($300\text{--}6000\text{ cm}^{-1}$) a Woollam IR-VASE based on Fourier transform spectroscopy was employed with resolution set to 4 cm^{-1} , while for photon energies between 0.5 and 6.5 eV, a Woollam VASE with autoretarder was used. There, the resolution was chosen to be better than 5 nm. The angle of incidence was varied between 46° (60°) and 74° in steps of 7° for the visible-ultraviolet (infrared) instrument. Ellipsometric parameters Ψ and Δ were recorded for every photon energy and angle of incidence. In the higher energy range between 5 and 20 eV, an ellipsometer installed at the insertion device

FIG. 1. Point-by-point fitted ellipsometric parameters Ψ and Δ of the α -Ga₂O₃ sample for three different angles of incidence in the spectral range corresponding to lattice phonons. Experimental data are shown as black continuous curves; the fits are drawn as red dashed curves.

beamline of the Metrology Light Source (MLS) in Berlin, Germany was used [55]. The angle of incidence was set to 67° there. Spectra recorded at the synchrotron are not limited by resolution but by energy step width, which was set to 20 meV up to 10 eV and to 50 meV up to 20 eV. All studies were performed at room temperature.

The corundumlike crystal structure of α -Ga₂O₃ determines a dielectric tensor of the form

$$\bar{\epsilon} = \begin{pmatrix} \epsilon_{1,\perp} + i\epsilon_{2,\perp} & 0 & 0 \\ 0 & \epsilon_{1,\perp} + i\epsilon_{2,\perp} & 0 \\ 0 & 0 & \epsilon_{1,\parallel} + i\epsilon_{2,\parallel} \end{pmatrix}. \quad (1)$$

The (0001) surface of the samples allows sensitive experimental access to $\bar{\epsilon}_\perp$ only, where $\perp$ represents the electric field vector oriented perpendicular to (0001). $\bar{\epsilon}_\perp$ is also called ordinary dielectric function. To measure the extraordinary dielectric function $\bar{\epsilon}_\parallel$, other sample surfaces than (0001) would be required.

The ordinary dielectric function was obtained by fitting Ψ and Δ data from all angles of incidence together in a multilayer model [56], which also accounts for the surface roughness via the Bruggeman effective medium approximation [57] and for the (0001)-oriented α -Al₂O₃ substrate. The dielectric functions published by Malitson and Tomiki *et al.* [58,59] for the visible-ultraviolet spectral range were used to describe the sapphire substrate. In the infrared spectral range, we determined experimentally the dielectric response of

FIG. 2. Point-by-point fitted ellipsometric parameters Ψ and Δ for five different angles of incidence below 6.6 eV. Experimental data are shown as black continuous curves; the fits are drawn as red dashed curves.

FIG. 3. Point-by-point fitted ellipsometric parameters Ψ and Δ from the synchrotron ellipsometer. Experimental data are shown as black continuous curves; the fits are drawn as red dashed curves.

sapphire on polished sapphire substrates with different surface orientations, i.e., (0001), (1 $\bar{1}$ 00), and (11 $\bar{2}$ 0) orientations.

After modeling the experimental data by superposition of different Kramers-Kronig consistent model functions optimized to match the experimental line shapes, a numerical point-by-point fit was performed without *a priori* assumptions on the line shape of $\bar{\epsilon}_{\perp}$. The excellent agreement of this point-by-point fitted model with the experimental data is displayed in Figs. 1, 2, and 3 for the different spectral ranges.

III. AB INITIO CALCULATION OF THE INFRARED-ACTIVE MODES

The frequencies of the infrared-active modes of α -Ga₂O₃ were calculated using a plane-wave pseudopotential approach to density functional theory (DFT) as implemented in the ABINIT code [60]. The calculations were performed in the local density approximation (LDA) using the Perdew-Wang parametrization of the exchange interaction and Troullier-Martins pseudopotentials. The 3d electrons of Ga were included as valence states. A $4 \times 4 \times 4$ Monkhorst-pack k -point sampling and a plane-wave basis set with an energy cutoff of 95 Ha were used. A full structural relaxation of the α -Ga₂O₃ unit cell was carried out, and the hexagonal lattice parameters $a = 5.004$ Å and $c = 13.410$ Å were obtained, in excellent agreement with the reported high-resolution x-ray diffraction

value ($a = 4.983$ Å and $c = 13.433$ Å) [54]. Phonon frequencies were determined by diagonalizing the dynamical matrix derived from the perturbation theory linear response approach [60]. The calculated frequencies of the zone-center infrared-active phonons are listed in the first column of Table I.

IV. RESULTS AND DISCUSSION

A. Infrared dielectric function

For the infrared dielectric function, we use a sum of Lorentzian oscillators and the dielectric limit to describe the point-by-point fitted experimental result. Therefore,

$$\epsilon_{\text{IR}}(\omega) = \epsilon_{\infty} + \sum_l \frac{S_l \omega_{\text{TO},l}^2}{\omega_{\text{TO},l}^2 - \omega^2 - i\omega\gamma_{\text{TO},l}} \quad (2)$$

is used for the ordinary and extraordinary dielectric functions, separately. The space group of corundum crystals is D_{3d}^6 ($R\bar{3}c$) expressing a ditrigonal-scalenohedral symmetry. At Γ , there are two infrared-active phonon modes with A_{2u} symmetry for the extraordinary dielectric function and four modes with E_u symmetry for the ordinary one.

The α -Al₂O₃ substrate has the same symmetry, and the corresponding experimental phonon modes are listed in Table I. Its dielectric limits are found to be $\epsilon_{\infty,\perp} = 3.08$ and $\epsilon_{\infty,\parallel} = 3.05$ from model fits. We note that synthetic sapphire was extensively investigated earlier with nearly identical results [61]. However, a more complicated anharmonic product description of the infrared part of the dielectric function was used there [62] which is not required in the present study.

For α -Ga₂O₃ our experimental geometry is only sensitive to the ordinary component of the dielectric tensor. For a proper data modeling routine, we therefore have to make an assumption about the extraordinary part of the dielectric tensor, i.e., the characteristic energy $\omega_{\text{TO},l}$, broadening factor $\gamma_{\text{TO},l}$, and amplitudes S_l of the two A_{2u} modes. For this purpose, we carefully compared the energy positions of Raman active phonon modes of α -Al₂O₃ and α -Ga₂O₃, which are fully explored [39,63]. Next, the results for the ordinary dielectric functions of α -Al₂O₃ and α -Ga₂O₃ were compared.

TABLE I. Calculated (first column) and experimentally obtained IR parameters (other columns). Values in italic were fixed and not fitted. ω_{TO} is the phonon mode resonance energy, γ_{TO} its broadening parameter, and S the corresponding amplitude factor. l is used for indexing the different E_u and A_{2u} symmetry phonon modes in both materials.

	Calc.			Experimental			
	α -Ga ₂ O ₃			α -Al ₂ O ₃			
	$\omega_{\text{TO},l}$ (cm ⁻¹)	$\omega_{\text{TO},l}$ (cm ⁻¹)	$\gamma_{\text{TO},l}$ (cm ⁻¹)	S_l	$\omega_{\text{TO},l}$ (cm ⁻¹)	$\gamma_{\text{TO},l}$ (cm ⁻¹)	S_l
E_u							
1	220				384.8	4.30	0.28
2	326	333.4	14.5	4.45	439.5	3.64	2.94
3	462	469.9	18.0	3.00	569.1	4.78	3.13
4	551	562.7	16.2	0.11	633.4	6.17	0.19
A_{2u}							
1	269	280	20	12	396.7	3.16	6.73
2	531	544	20	1	582.7	2.95	1.71

FIG. 4. Comparison of characteristic energies of phonon modes of α -Al₂O₃ and α -Ga₂O₃. Raman active phonon modes were taken from Refs. [63] and [39], and the infrared-active modes of sapphire were taken from Ref. [61]. The three missing infrared-active phonon modes are extrapolated from the linear relationship and their frequencies are displayed in the graph.

Finally, the phonon frequencies computed by first-principles calculations (see Sec. III) were also taken into account.

In Fig. 4, we compare the characteristic phonon energies of α -Al₂O₃ and α -Ga₂O₃ and a linear relationship is fitted to the data. From this linear dependence, the three missing infrared-active phonon modes are determined to be around 231 cm⁻¹ ($E_{u,1}$), 247 cm⁻¹ ($A_{2u,1}$), and 480 cm⁻¹ ($A_{2u,2}$). Note that the slope of the interpolation line (1.26) matches approximately the square root of the reduced mass ratio of Ga₂O₃ and Al₂O₃ (1.19). However, for use in our model fits, we iteratively changed the extracted A_{2u} phonon energy positions to improve the agreement (Fig. 1). We finally assumed the values of 280 and 544 cm⁻¹, as reported in Table I in italic. These values are also in good agreement with computational results (Sec. III and Table I) which systematically underestimate the experimentally obtained room temperature phonon mode frequencies. The order of phonon mode amplitudes is basically maintained when going from α -Al₂O₃ to α -Ga₂O₃. The broadening factors are substantially higher for the thin epitaxial α -Ga₂O₃ film, because it is expected to contain a density of point and structural defects larger than that of the high-quality bulk sapphire substrates investigated. For the remaining E_u phonon mode of α -Ga₂O₃, a reliable experimental estimate cannot be given because this phonon is found far from the spectral range of our measurements.

Our analysis of the dielectric function for the E_u phonon modes of α -Ga₂O₃ allows us to unambiguously assign three of the four E_u modes. The missing undetectable mode is expected to have low amplitude $S \approx 0.1$ and a characteristic energy < 275 cm⁻¹, which is in agreement with the computational result of 220 cm⁻¹. Figure 5 presents a comparison of the point-by-point fitted experimental dielectric function of α -Ga₂O₃ to the model given by Eq. (2). No significant residual contributions from neither substrate modes nor the extraordinary phonon modes are detectable, which corroborates the validity of the assumptions we made for the A_{2u} modes. The ordinary dielectric limit of α -Ga₂O₃ is found to be $\epsilon_{\infty,\perp} = 3.75$ from our model fits. Maintaining the ratio of ordinary and

FIG. 5. Ordinary dielectric functions of α -Ga₂O₃ (upper panel) compared to α -Al₂O₃ (lower panel). The real parts are drawn in blue, and the imaginary parts in red. Continuous curves represent model functions, while the point-by-point fitted data are drawn as open circles for α -Ga₂O₃. There is a systematic shift to lower energies from α -Al₂O₃ to α -Ga₂O₃, while amplitude ratios are approximately maintained.

extraordinary dielectric limits from the theoretical calculations published in Ref. [17] of ~ 1.03 , we obtain $\epsilon_{\infty,\parallel} = 3.64$. Please note that for both corundum materials, $\epsilon_{\infty,\perp} > \epsilon_{\infty,\parallel}$, which implies that these materials have a negative birefringence.

B. Optical properties in the visible-to-ultraviolet spectral range

The complex ordinary dielectric function of α -Ga₂O₃ is shown in Fig. 6 for the range of photon energies from 0.5 up

FIG. 6. Ordinary dielectric function of α -Ga₂O₃ from point-by-point fits to experimental data in the spectral region between 0.5 and 20 eV.

TABLE II. Parameter set for the empirical description of $\varepsilon_{1,\perp}$ below 4.8 eV at $T = 295$ K.

E_G (eV)	5.8
E_H (eV)	11.1
A_G	1.3
A_H (eV)	38.5

to 20 eV. Experimental point-by-point fits were performed on data obtained by using two ellipsometers as described above. First of all, we note that the imaginary part of the dielectric function ε_2 is not zero for photon energies higher than ~ 5.6 eV. This is the onset of strong interband absorption of the material associated with the direct band gap. The shape, temperature dependence, and derivation of the exact energy value of the direct band gap was discussed in detail recently [41]. The major findings were the determination of a fundamental direct band gap at 5.61 eV and a higher energy transition at 6.44 eV. An exciton binding energy of about 110 meV was deduced. Both absorption steps are clearly visible in Fig. 6 in the ε_2 spectrum and in the corresponding Kramers-Kronig maxima in the ε_1 spectrum.

The refractive index n is equal to $\sqrt{\varepsilon_1}$ in the energy range where $\varepsilon_2 = 0$, i.e., for photon energies below the band gap. An analytical description of the point-by-point fitted $\varepsilon_{1,\perp}(\hbar\omega)$ can be made using the model proposed by Shokhovets *et al.* [64]:

$$\varepsilon_1(\hbar\omega) = 1 + \frac{2}{\pi} \left(\frac{A_G}{2} \ln \frac{E_H^2 - (\hbar\omega)^2}{E_G^2 - (\hbar\omega)^2} + \frac{A_H E_H}{E_H^2 - (\hbar\omega)^2} \right). \quad (3)$$

It is derived by a Kramers-Kronig transformation of a representative simplified model for $\varepsilon_2(\hbar\omega)$ consisting of a constant value A_G for ε_2 above the effective absorption onset E_G and an upper energy contribution given by a δ function at E_H weighted by A_H representing effective high-energy contributions. By fitting Eq. (3) to $\varepsilon_1(\hbar\omega < 4.8$ eV), we obtain the parameters given in Table II. In this model, the dielectric limit ε_∞ can be found as the asymptotic limit at $\hbar\omega \rightarrow 0$ of Eq. (3), and we obtain $\varepsilon_\infty = 3.75$. This value is in perfect agreement with $\varepsilon_{\infty,\perp}$ derived from the infrared analysis (see above).

The high-energy interband excitonic transitions are visible as peaks in $\varepsilon_2(\hbar\omega)$. We expect a certain similarity between the observed features and those of α -Al₂O₃ because the crystal symmetry plays a major role in shaping the band structure. Substitution of Ga for Al in the corundum sesquioxide is expected to decrease transition energies. Similar behavior is reported for β sesquioxides [20] or when comparing AlN and GaN, both in the zinc-blende [65] and in the wurtzite polytype [66]. Also the classical III-V zinc-blende semiconductors AlAs and GaAs show a similar behavior [67].

The high-energy interband transitions of sapphire were reported for a very wide spectral range [59,69,70]. Here, we use the experimental results by Tomiki and colleagues [59] and follow a later analysis by Harmann *et al.* [68], where six characteristic transition energies were identified in the spectral range up to 18 eV for the ordinary dielectric function (Table III). Visual inspection of ε_2 for α -Ga₂O₃ shows that the overall line shape is quite similar (Fig. 7). We therefore assign high-energy transition peaks following

TABLE III. Characteristic energies of high-energy transitions of the ordinary dielectric functions of α -Ga₂O₃ and α -Al₂O₃ [68].

E_k k	Ga ₂ O ₃ (eV)	Al ₂ O ₃ (eV)
1	5.60	9.25
2	6.44	10.88
3	9.70	12.37
4	11.18	13.32
5	12.79	14.91
6	15.37	17.40

the identification performed for sapphire [68]. The first six characteristic transition energies are summarized in Table III.

The similarities in shapes and amplitudes (Fig. 7) of the identified high-energy features lead us to a tentative one-to-one correlation of the related features for both materials. Accordingly, the arrows shown in Fig. 7 correlate the characteristic transition bands of both materials. Several attempts were made to assign the observed bands of the dielectric function of sapphire to different regions of the band structure in a simplified atom orbital picture [70,71]. The dominant contributions in ε_2 of α -Al₂O₃ are believed to originate mainly from transitions between O2p valence bands and Al3p conduction bands [70]. Recent first-principles results of different Ga₂O₃ polytypes [17] yield a similar assignment for the two main absorption contributions in α -Ga₂O₃. The transitions $k = 3$ and 4 (Table III) are therefore tentatively assigned mainly to transitions between O2p valence bands and Ga4s/4p conduction bands.

These assignments are further corroborated by comparing the theoretically calculated dielectric function including Coulomb interaction [17] of α -Ga₂O₃ with our experimental result (Fig. 8). The overall line shape of our experimental result is nicely reproduced by the computational spectrum. However, the theoretical curve is found at lower energies compared to the experimental spectrum with higher discrepancies at higher

FIG. 7. Comparison of the ordinary imaginary parts of the dielectric functions of corundum Al₂O₃ (blue, lower curve) and Ga₂O₃ (red, upper curve). The overall similarities between their respective line shapes is obvious. The arrows indicate a one-to-one match of high-energy transition bands.

FIG. 8. Comparison of experimental imaginary part of the ordinary dielectric function of α -Ga₂O₃ with the calculated theoretical result from Ref. [17].

energies. Most likely, this fact originates from a slight underestimation of the quasiparticle corrections and/or screening effects. Nevertheless, the overall agreement visible in Fig. 8 allows one to conclude that the general findings of Ref. [17] can describe correctly the optical spectra of α -Ga₂O₃.

V. SUMMARY AND CONCLUSIONS

Spectroscopic ellipsometry measurements on the metastable α phase of Ga₂O₃ have been performed over an extended energy range up to 20 eV. The ordinary dielectric function $\bar{\epsilon}_{\perp}$ has been determined by point-by-point fitting of the ellipsometry data without *a priori* assumptions on the $\bar{\epsilon}_{\perp}$ line shape. Excellent agreement with the experimental

data is achieved. The infrared dielectric function is accurately described with a sum of Lorentzian oscillators, which has allowed us to clearly identify three out of the four expected E_u infrared-active modes at frequencies of 333.4, 469.9, and 562.7 cm⁻¹. These frequencies are in good agreement with theoretical values of infrared-active modes that we have calculated using a DFT approach.

The dielectric function in the ultraviolet below the absorption onset was analyzed using Shokhovets' model, and the dielectric limit $\epsilon_{\infty} = 3.75$ found is in perfect agreement with the value derived from the infrared data. The high-energy interband excitonic transitions are clearly visible as peaks in $\epsilon_2(\hbar\omega)$. These have been tentatively identified by analogy with the well-characterized α -Al₂O₃ interband transitions by establishing a one-to-one correspondence between the peaks observed in their respective absorption spectra. Our analysis suggests that the observed absorption peaks originate mainly from O2p valence band to Ga4s/4p conduction-band transitions.

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