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Which direction is uphill? Scattering of He atom grazing-angle diffraction beams from surface steps

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Abstract

Diffraction beams from the scattering of He atoms from the Rh(3 1 1) surface were observed at scattering angles of up to grazing exit at 90° with respect to the surface normal. Under grazing exit conditions, a broad scattered signal appears which is interpreted as diffuse scattering of the grazing diffraction beam arising from collisions with the low density of step defects resulting from the small miscut of the crystal. This experiment opens new possibilities for the characterization of surface defects with diffraction techniques. © 2001 Elsevier Science B.V. All rights reserved.

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Regardless of the degree of cleanliness or the care in preparation, all surfaces include a variety of intrinsic defects which play a large role in the way in which a surface interacts with its environment. Primary among these intrinsic defects are steps in the otherwise ordered surface, and there are many ways of detecting these steps including reflection high energy electron diffraction (RHEED), X-ray diffraction, and scanning tunneling microscopy (STM). It has also been demonstrated that surface imperfections can be characterized through careful analysis of the weak background intensities of scattered atoms [1,2] or electrons [3] between the diffraction peaks. Recently, a new method has been developed for observing intrinsic surface defects via scattering of the well-defined two-dimensional atomic diffraction beam parallel to the surface under bound state resonance (selective adsorption) conditions [4,5]. In this paper, we report on the observation of a characteristic signal due to scattering of atoms from surface defects under conditions of grazing exit diffraction, in which the diffraction beam is directed very nearly parallel to the surface.

In diffraction from an ordered periodic surface there are interesting effects which should occur whenever a diffraction beam is at grazing exit conditions, where it makes the transition from an evanescent wave to a real diffracted beam. These effects include the threshold resonance [6–8], skipping phenomena and the onset of classical chaos [9]. Several earlier experiments using He atom diffraction attempted to follow the intensity of selected diffraction beams as they passed through

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grazing exit conditions and into the evanescent state, but these experiments gave inconclusive results because the beams could not be reliably observed for final scattering angles greater than about $\theta_f \approx 85°$ [10,11]. In this letter we describe a new series of experiments which exploits well-defined incident He atom beams and a very well characterized metal surface which allowed the measurement of diffraction beams all the way to $\theta_f = 90°$.

The crystal sample was a well ordered Rh(3 1 1) surface with a miscut of less than 0.3° which implies that the average (3 1 1) terrace length between step defects is ≈200–300 Å. The topmost layer of the Rh(3 1 1) is a corrugated surface of parallel close-packed rows separated by 4.455 Å [12]. For several incident beam energies and for several different diffraction orders, it was found that the diffraction beam intensity near grazing exit decreased approximately linearly as a function of $90° - \theta_f$. Very near to grazing exit conditions, a broad peak in the background intensity was observed, and this peak was considerably larger when the diffraction beam was exiting in the direction that would cause it to collide with the riser faces of the step defects caused by the miscut (i.e., the "upstairs" direction as illustrated at the top of Fig. 2). A similar peak, but of much smaller intensity, was observed when the crystal was rotated by 180° and the diffraction beam exited in the "downstairs" direction in which it encounters far fewer step risers. The intensity of the peak decreased rapidly with increasing azimuthal angle away from the plane perpendicular to the steps, and disappeared when the crystal azimuth was rotated by as much as 10°. This broad background peak is found to agree well with a theoretical model of Fraunhofer scattering from a step edge when the interference with the back-reflected beam from the large terraces is taken into account.

In the experimental apparatus, discussed in detail in Ref. [13], the incident He atom beam is generated by a supersonic nozzle with gas pressures between 60 and 80 bar and He translational energies E_i between 25 and 180 meV. After passing through skimmers the angular dispersion of the beam incident onto the target crystal is less than 0.4°. The crystal sample was oriented with X-ray diffraction, cut parallel to the (3 1 1) plane with a wire saw and afterwards mechanically polished and electropolished. After placement in the UHV chamber the crystal was further prepared by several cycles of sputtering with 1.0 keV Ne ions and heating up to 1100 K, and by high temperature treatments in oxygen and hydrogen. The cleanliness of the sample was judged by the integral intensity and sharpness of the diffraction peaks and by the ability to reproduce the known data for the low-coverage hydrogen phases [14] which are very sensitive to the presence of impurities on the surface. The measurements were performed with the crystal sample temperature at 100 K. All data presented here refer to a scattering geometry in which the He beam impinges perpendicular to the close-packed rows of the Rh(3 1 1) substrate. The orientation of the crystal in both polar and azimuthal angles was determined to better than 0.2° through measurement of the diffraction peak position on both clean and H-covered surfaces.

Fig. 1 is a graph of all observable diffraction beam intensities as a function of incident polar angle θ_i, measured with respect to the normal to the (3 1 1) surface, for a He atom beam of wavelength $\lambda = 0.56$ Å ($E_i = 63$ meV). The intensity shown is the integrated area of each diffraction peak. At this incident energy, the (0 1) beam disappears and becomes evanescent at the critical incident angle $\theta_i = \theta_c = 60.8°$. It is evident that the intensity of the (0 1) diffraction peak is very nearly linear in the angular distance from the critical angle $\theta_i - \theta_c$ for more than 10° before disappearing. There is no evidence of a threshold resonance in the neighborhood of θ_c which would be manifest by a sharp decrease in intensity.

Fig. 2 shows in more detail the observed scattered intensity as a function of θ_f in the vicinity of 90° for several incident angles near $\theta_i = \theta_c$ for the (0 1) diffraction order. Two incident energies are shown, the upper two panels are for $\lambda = 0.56$ Å for which $\theta_c = 60.8°$ and the lower panels are for $\lambda = 0.8$ Å ($E_i = 30$ meV) where $\theta_c = 55.3°$. For each incident energy the panel on the left is for the (0 1) diffraction beam pointing in the "upstairs" direction (as illustrated in the insert at the top of Fig. 2) and the panel on the right is for the "downstairs" configuration. There is a broad peak which remains nearly stationary at very nearly the

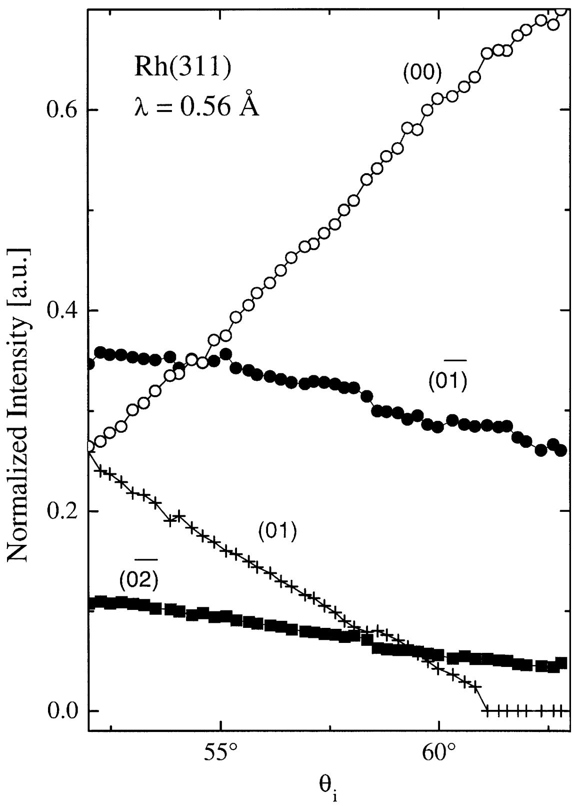

Fig. 1. Integrated intensities of the diffraction peaks as a function of incident polar angle for a He atom beam of wavelength $\lambda = 0.56$ Å ($E_i = 63$ meV) impinging on a Rh(3 1 1) surface.

same value of θ_f which becomes less intense as θ_i approaches θ_c, and disappears for $\theta_i > \theta_c$. What is striking, however, is that this peak is much larger in the "upstairs" direction than for the "downstairs" direction. For similar values of θ_i close to θ_c, the intensity in the "upstairs" direction is approximately an order of magnitude larger.

This anomalously large scattering signal in the "upstairs" direction is interpreted as scattering of the He atoms out of the (0 1) diffraction beam caused by collisions with the faces of the step defects produced by the slight miscut of the surface. Because of the miscut, a systematic error is induced in the surface which causes many more step riser faces to appear in the "upstairs" direction than in the "downstairs" direction, hence the large differences in observed intensity in the two opposing scattering directions.

This large discrepancy in the two crystal azimuthal orientations (i.e., with the steps oriented either 90° or 270° with respect to the scattering plane) cannot be due to a correspondingly large difference in the intensity of the grazing angle (0 1) diffraction peak in these two opposing configurations. On Rh(3 1 1), this is verified both by our direct measurements, which show negligible differences in diffraction beam intensities for the two directions, and by elastic close coupling calculations using the known potential for this surface [16], which predict that the differences in diffraction intensities in the two orientations are no more than 10%. If there were large differences in diffraction intensities for the two different orientation configurations, this would require a significant asymmetry within the unit cell of the periodic corrugation of the Rh(3 1 1) terraces. However, it is well known that symmetric corrugation functions are adequate to describe He-diffraction even for seemingly asymmetric stepped surfaces like the Ni(115), Cu(3 1 1) and Cu(112) [15].

Another possible alternative explanation is that the anomalous intensity seen in Fig. 2 is due, not to scattering from a grazing diffraction beam, but to scattering from an evanescent diffraction beam. The evanescent beams have wave vectors with a real component oriented parallel to the surface, and amplitudes that decay exponentially in the perpendicular direction. Because of the small energy and angular spread of the incident beam, the (0 1) diffraction peak at grazing angles will be partly evanescent. However, the possibility of scattering from the evanescent part of the (0 1) beam or from any other evanescent beam can be ruled out because simple calculations show that the short-range exponential decay of an evanescent beam away from the surface would cause its defect scattering intensity to decrease much faster for $\theta_i > \theta_c$ than is observed in Fig. 2.

The expected scattered intensity distribution can be discussed in terms of relatively simple models based on Fraunhofer diffraction. The grazing exit diffraction beam near the critical angle can be viewed as a plane wave traveling parallel to the surface with a wave vector of magnitude $|\mathbf{K}_i + \mathbf{G}| \approx k_i$, where $\mathbf{K}_i$ is the component of the incident wave vector k_i parallel to the surface ($\mathbf{K}_i = k_i \sin\theta_i$)

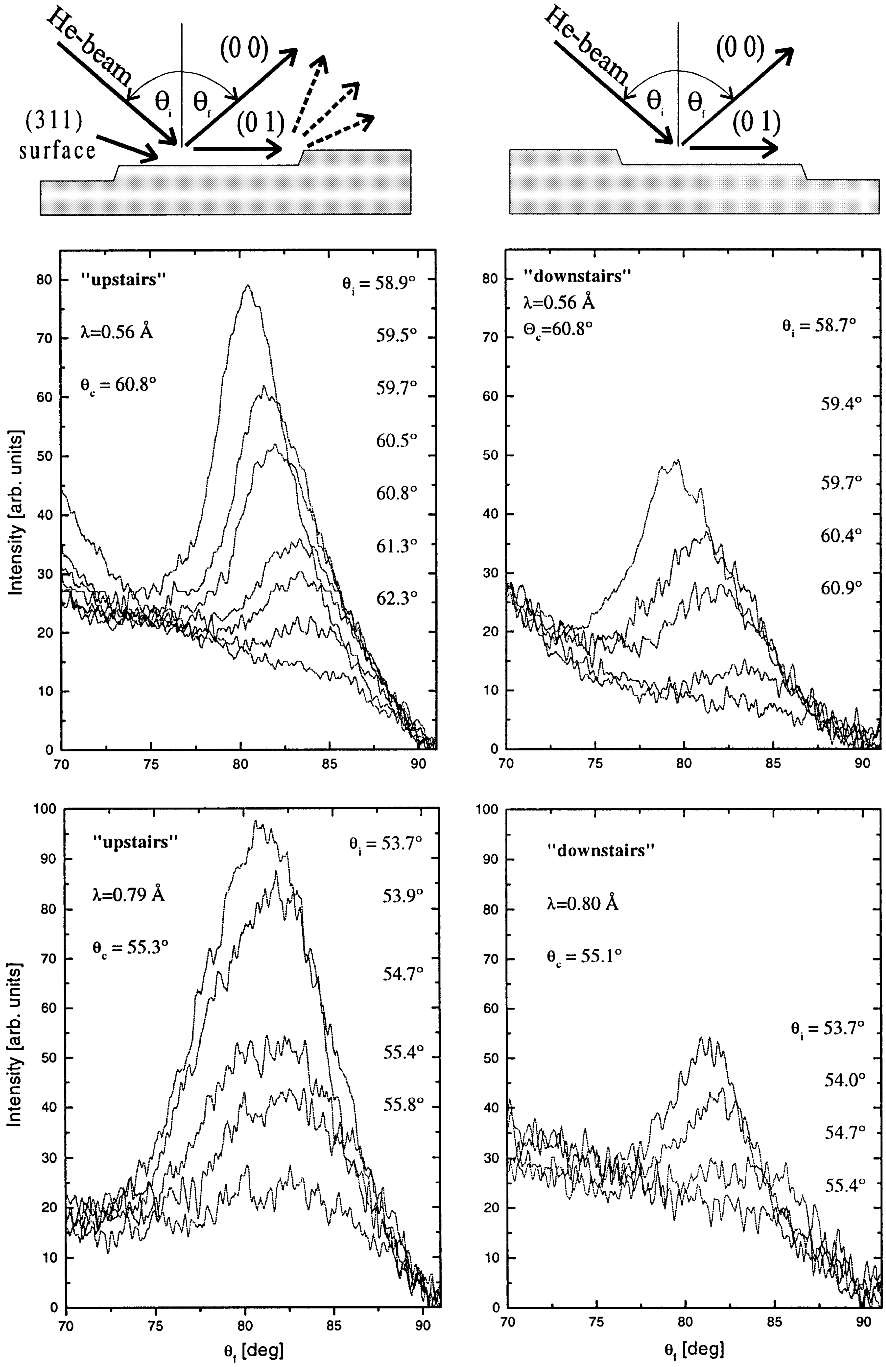

Fig. 2. Measured scattered intensity amplitudes from the (0 1) diffraction beam as a function of final angle θ_f for several incident angles θ_i very near the critical angle for the disappearance of the (0 1) diffraction peak. Two different He atom energies and the two opposing crystal directions are shown.

and **G** is the surface reciprocal lattice vector of magnitude $G = 2\pi/d$, where $d = 4.455$ Å is the corrugation period.

The simplest approach to scattering from a step face defect of height a is to model it by the Fraunhofer diffraction pattern for a linear obstacle. However, when the diffraction beam strikes the step defect it is scattered both toward and away from the surface. That part of the scattered amplitude which is scattered towards the surface will be reflected back by the terrace at the top of the step, and this back-reflected amplitude will interfere with the directly scattered part to give rise to an observable signal.

According to Babinet's principle, the scattering amplitude from an opaque obstacle can be replaced by a similarly shaped slit in an opaque sheet. The angle that the step riser face makes with the surface plane is not important at this level of approximation, and the scattering amplitude is the standard Fraunhofer expression

$$A(\kappa) = \frac{2A_0}{\kappa} e^{-i\kappa a/2} \sin(\kappa a/2), \quad (1)$$

where A_0 is the amplitude of the diffraction beam and $\kappa = k_i \cos\theta_f$. Including the back-reflection from the mirror surface implies that the total scattering amplitude is given by $A_T(\kappa) = A(\kappa) - e^{2i\kappa b} A(-\kappa)$, where the parameter b in the phase factor is the height chosen for the plane of reflection relative to the terrace plane at a distance $z = a$ above the surface. The simplest and most logical choice for the position of the reflecting plane is to make it coincident with the top of the terrace which corresponds to $b = 0$ leading to the following expression for the scattered intensity:

$$I(\theta_f) \propto \frac{I_{01}}{\kappa^2} \sin^4\left(\frac{\kappa a}{2}\right), \quad (2)$$

where I_{01} is the intensity of the (0 1) diffraction beam given by $I_{01}(\theta_i) = (\cos\theta_f/\cos\theta_i)|A_{01}|^2$. Elastic coupled channels calculations using the well established He–Rh(3 1 1) potential [16] show that the amplitude A_{01} for the (0 1) beam is nearly constant in the region of the critical angle, thus the linear dependence of $I_{01}(\theta_i)$ as exhibited in Fig. 1 is explained by the θ_f dependence of the flux factor $\cos\theta_f/\cos\theta_i$.

Fig. 3 shows the comparison of the experimentally measured data with the intensity predictions of Eq. (2). The data is the same as shown in Fig. 2, after subtracting a linear background. The theoretical curves are calculated with a value of $a = 2.28$ Å which is exactly twice the minimum step height expected for the fcc(3 1 1)surface. The relative intensities of the theoretical curves at each value of θ_i are determined from the observed linear dependence of the (0 1) diffraction peak intensity for $\theta_i < \theta_c$ and by assuming that the incident beam has a Gaussian distribution in angular spread about its center, both in and out of the scattering plane. The full width at half maximum (FWHM) of the Gaussian is chosen to be the measured FWHM of the specular beam which is $\sigma = 1.85°$. The FWHM of the specular beam is substantially larger than that of the incident beam because of the proximity of the detector to the crystal, the source-to-crystal distance being approximately 0.5 m while the detector is only 4.0 cm from the sample. Thus, the intensity $I_{01}(\theta_i)$ is chosen according to the formula

$$I_{01}(\theta_i) = \frac{S}{\sqrt{\pi}\sigma} \int_{-\infty}^{\theta_c - \theta_i} e^{-\theta^2/\sigma^2} (\theta_c - \theta_i - \theta)\, d\theta. \quad (3)$$

For θ_i sufficiently smaller than θ_c, $I_{01}(\theta_i)$ of Eq. (2) is a linear function and the slope coefficient S is chosen so that it agrees with the measured intensity of the (0 1) beam such as shown in Fig. 1. However, for θ_i close to, or even slightly larger than θ_c, $I_{01}(\theta_i)$ of Eq. (3) accounts for the fact that, although the leading edge of the incident beam distribution is greater than θ_c, the trailing edge still produces a real diffraction intensity.

In both the upstairs and downstairs directions, Fig. 3 shows good agreement between the observed scattering distribution and the theoretical model of Eq. (2) for values of θ_i ranging from slightly less than θ_c, to somewhat larger than θ_c where only the trailing portion of the incident beam distribution produces a real (0 1) diffraction beam. The shape of the curve, the stationary position of the maximum for all θ_i, and the intensity are all well predicted for a value of a which is twice

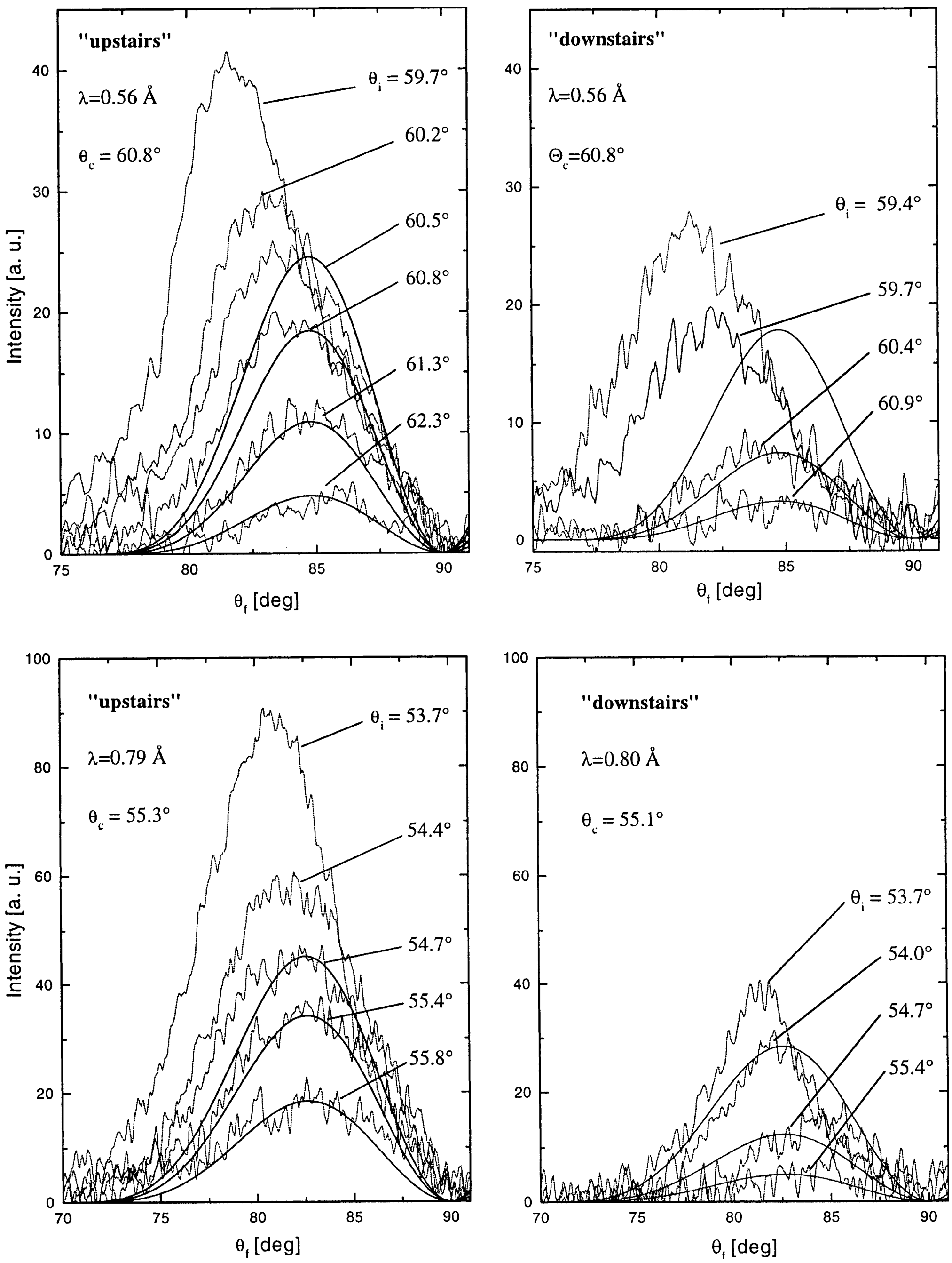

Fig. 3. The same data as shown in the "upstairs" and "downstairs" panels of Fig. 2, after background subtraction, are compared with theoretical predictions (smooth solid curves) of the scattered intensity due to scattering from widely spaced step face defects.

the minimum step height. However, the nearly order-of-magnitude difference in intensity near $\theta_i \approx \theta_c$ indicates a similar difference in density of step risers in the two orientations.

The minimum step height on the fcc(3 1 1) surface is $a = 1.14$ Å. A defect with exactly twice this value could be indicative of double-height steps, or of defects consisting of a "mini-facet" of two adjacent single steps. The present theoretical model would give the same results for both cases. Concerning single steps, which in addition to double steps have been shown to be present at this surface [17], our model predicts that they would produce a much broader feature than double steps, centered at $\sim 73°$ in Fig. 3. As a consequence, this signal could not be distinguished from the background in our experiments.

To conclude, we would like to discuss some future possibilities for application of this effect. (i) The quantitative study of grazing exit diffraction will enable measuring the differential and total cross sections of surface defects under the well-defined conditions of an illuminating beam travelling parallel to the surface. (ii) There are some intriguing possibilities for inelastic scattering effects. If the surface is contaminated with adsorbates having low energy modes, such as frustrated translation modes [18], there should be inelastic Einstein mode multiquantum overtones scattered out in all directions by these defects. We would expect the grazing exit diffraction beam to impart large parallel momentum transfers and hence produce large inelastic intensities. (iii) This effect is not limited to atom or molecule scattering, it should be observed in electron scattering or any other scattering process in which the periodic surface produces diffraction beams which can have significant intensity near grazing exit conditions [19,20].

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