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Surface and Magnetic Orientation in a Type II Nematic Lyomesophase

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A type II nematic lyomesophase formed by a quaternary system (K decanoate/water/decanol/KCl) has been studied by X-ray diffraction (XD) and optical microscopy (OM) at room temperature. Samples in capillaries of various thicknesses, materials and geometries have been studied under the influence of wall effects, residual magnetic orientation and orientation in presence of magnetic fields. Results evidence that surface orientation extend typically up to 0.5 mm. The planar diffracting units have a characteristic distance in the director direction of 36 Å. The analysis of the compromise between surface and magnetic orientation by XD allowed to determine a critical field of 200 G for a 0.5 mm thickness; the elastic constant is estimated as 10^{-7} dynes. Analised by OM, the sample is axially positive, but shows also a weak biaxiality.

I. INTRODUCTION

X-ray diffraction results[1-3] on some specific nematic lyomesophases made of hydrocarbon amphiphile/water/additives (alcohol and/or salt) evidenced that the so-called[4] type II phases (with diamagnetic anisotropy $\Delta\chi < 0$) have lamellar disc micelles[1,2] while the type I phases (with $\Delta\chi > 0$) have cylindrical micelles.[2,3] These phases have also been called respectively N_L and N_C.

Although there has been increasing interest in these nematic lyomesophases in the last years,[5-7] few such systems have so far been studied by X-ray diffraction; particularly the compromise between surface and magnetic orientation on these nematic lyomesophases has been little explored, although evidence of unusual wall effects has been reported.[1,3]

In this paper we report the study by X-ray diffraction (XD) and optical microscopy (OM) of a type II nematic lyomesophase formed by a quaternary system with *K* decanoate at room temperature. Samples in capillaries of various thicknesses, materials and geometries have been studied under the influence of wall effects, residual magnetic orientation and orientation in presence of magnetic fields.

II. EXPERIMENTAL

The samples were prepared by usual methods[4,6] by the NMR laboratory of the Chemistry Institute, USP, with composition in weight *K* decanoate 35/water 52/decanol 8/KCl 5.

A small angle Rigaku-Denki diffractometer and a Laue camera, both with CuNi filtered radiation were used for XD. The samples, sealed in capillaries, were placed in vertical position with their axes perpendicular to the X-ray beam (XB) in a transmission geometry.

Quartz, lindemann and Na glass capillaries (mainly of 0.7 mm thickness) as well as pyrex glass capillaries of 2 mm and specially constructed glass and quartz capillaries with a conic form and thickness varying from 0.5 mm to 2 mm along a height of 3 cm have been used for XD measurements.

A small electromagnet (fields up to 800 G) has been projected and adapted to the X-ray diffractometer to allow measurements with $\vec{H}$ present in the equator direction (perpendicular to the XB and the capillary axis). Residual magnetic orientation has been obtained placing the sample in permanent magnets (2 and 14 KG), with $\vec{H}$ perpendicular to the capillary axis.

OM observations have been made in orthoscopic and conoscopic geometries with samples in planar capillaries 0.3 mm thick.

III. RESULTS AND DISCUSSION

Results are very similar to those obtained for another type II lyomesophase made of Na decyl sulfate.[1] A characteristic diffraction peak occurs at s values 0.028 Å^{-1}; the degree of sharpness and orientation of the diffraction peak varies considerably with the sample holder and the state of magnetic orientation. This diffraction corresponds to a characteristic distance between diffracting units (planar micelles in the form of discs or platelets) in the direction parallel to the director $\vec{n}$ of about 36 Å.

It shall be mentioned that the nature of the inner band[1,3] that appears weakly in thin samples and strong and dominant in thicker samples has been clarified by measurements made with monochromatic radiation:[8] it corresponds to white radiation since the CuK_α peak is strongly absorbed for samples with more than 1.5 mm thickness. However, the evidence for the formation of aggregates of micelles remains,[1,8] since the width of the diffraction peak indicates the existence of some degree of positional order. Detailed discussion of this point will be made in a forthcoming paper.

Regarding the effects of surface orientation, it is observed that in quartz capillary the diffraction reduces to a Bragg point in the equator indicating a director $\vec{n} \perp$ to the capillary axis; in lindemann glass capillary the diffraction is sharp but shows an arc around the equator evidencing a less perfect wall orientation and in Na glass the band becomes broader and with the same arc. The preferential direction along the equator could be explained either by $\vec{n}$ tangent to the walls in the plane $\perp$ to the capillary axis and a director field made of concentric rings or by $\vec{n} \perp$ to the walls and a radial director field. However, since the sample in planar glass plates shows the typical homeotropic pseudo-isotropic texture, we believe the condition $\vec{n} \perp$ walls should apply also to the cylindrical geometry and therefore Figure 1a is adopted as our model for surface orientation. This means that the diffraction from a capillary reveals essentially the structure in the plane $\perp$ XB that contains the capillary diameter.

The effects of magnetic orientation are observed in 2 mm thick samples with residual magnetic orientation as well as in thinner samples in presence of $\vec{H}$. In the geometry $G_{\parallel}$ ($\vec{H} \| \mathrm{XB}$) the diffraction peak appears in the equator while in the geometry $G_{\perp}$ ($\vec{H} \perp \mathrm{XB}$) no diffraction peak appears. These results evidence that wall effects are added to the magnetic orientation, which induces $\vec{n} \perp \vec{H}$, that is, $\vec{n}$ in the plane of the disc. Figure 1b shows a sketch of the situation for $\vec{H}$ above a critical value.

The absence of diffraction in the direction perpendicular to $\vec{n}$ indicates a rather large disc diameter. These results also coincide with those previously obtained in our laboratory[1] for another type II lyomesophase, but are in disagreement with results from another laboratory,[2] where in the geometry equivalent to $G_{\perp}$ another diffraction peak indicates a rather small disc diameter. This discrepancy is probably due to a problem of intensity, since this other diffraction is about 20 times weaker[9] than the observed one, and in this condition it could not be observed by us.

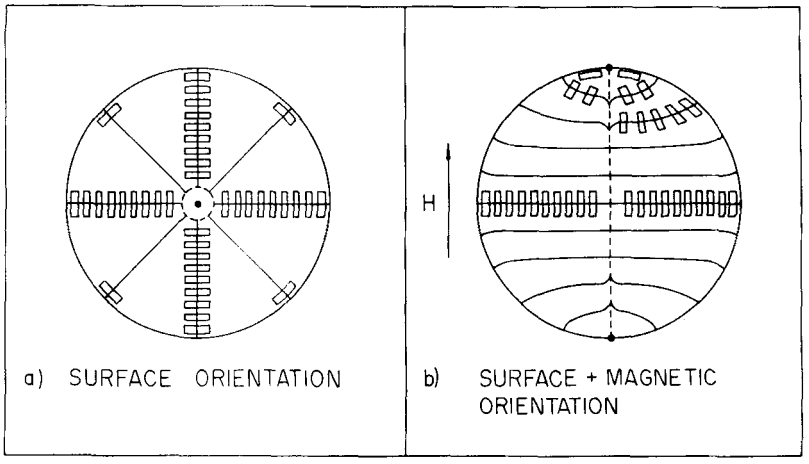

FIGURE 1 Diagrams showing surface and magnetic orientation in a plane perpendicular to the capillary axis, that contains both the directors and the magnetic field. The rectangles represent cross sections of the disc micelles.

Characterization of oriented samples is easily made by observing the sample between crossed polarizers. Samples with strong surface orientation (thin quartz capillary) are more transparent and show a line at the capillary axis, while unoriented samples are more translucid. Thick samples oriented in a magnetic field perpendicular to the capillary axis are transparent and present, when viewed with incident light $\| \vec{H}$, a translucid plane that contains the capillary axis and the magnetic field, dividing the sample in two half-cylinders; they show lines parallel to the capillary axis when viewed with incident light $\perp \vec{H}$. These observations are in agreement with the diagrams of Figure 1.

The effect of wall orientation has been mapped using the special conic capillaries and a thin punctual XB. Figure 2 shows XD results obtained with the point beam exploring different regions of the sample, along a horizontal line in a region of 1.8 mm thickness and along a vertical line in the central part of the capillary. It is seen that in the thicker part the diffraction band (due to white radiation) is oriented along the meridian perpendicular to the equator at the centre of the sample; this type of orientation is induced by the interface with air. As the wall is approached, the orientation changes continuously in the direction of the equator; these results evidence that wall effects extend up to ~ 0.5 mm in lyotropic nematics. Figure 3 shows a diagram of the director field in the conic capillary that gave XD results of Figure 2.

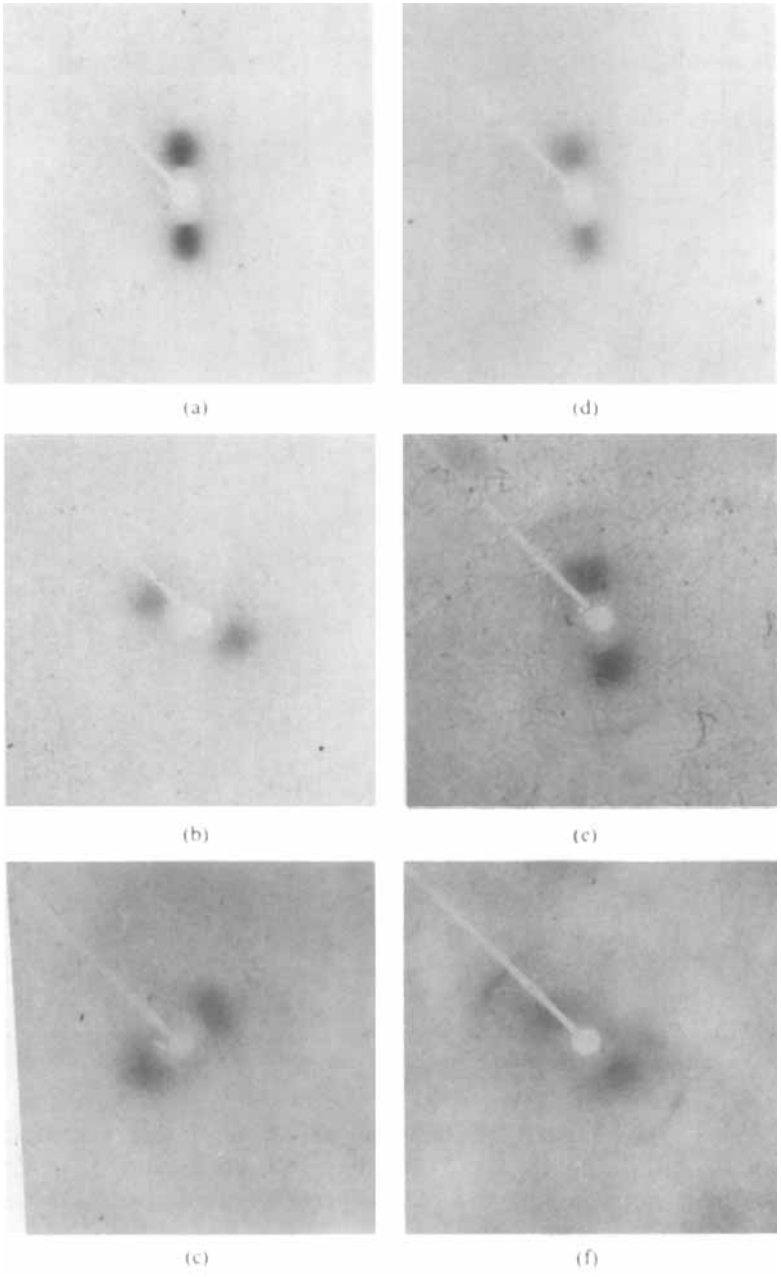

FIGURE 2 Mapping of a sample in a conic capillary by XD: (a) Centre at 1.8 mm thickness. (b) Distance of 0.2 mm from the wall on one side at 1.8 mm thickness. (c) Distance of 0.2 mm from the wall on the other side at 1.8 mm thickness. (d) Centre at 1.5 mm thickness. (e) Centre at 1.1 mm thickness. (f) Centre at 0.9 mm thickness.

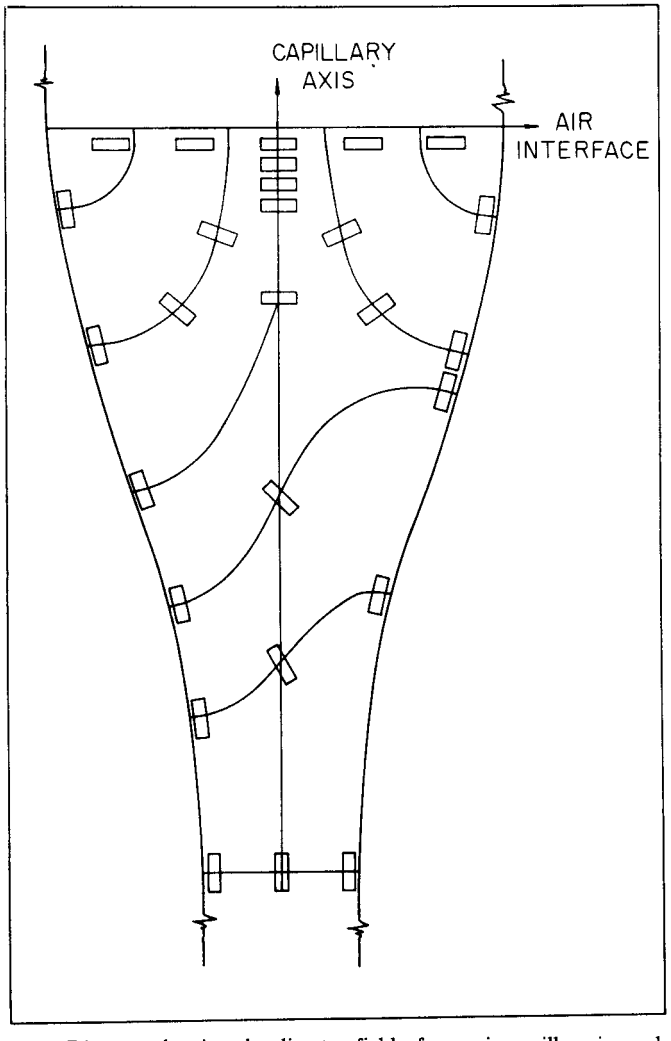

FIGURE 3 Diagram showing the director field of a conic capillary in a plane that contains the capillary axis. The rectangles represent cross sections of the disc micelles.

Usually the equatorial orientation is lost only very near the interface with the air; the thickness of the layer with orientation $\perp$ to the equator is not constant and may depend on the degree of water evaporation at this surface.

Figure 4 shows a typical texture observed by OM in the conic glass capillary, with a surface discontinuity in the director field. The texture of the upper part is typical for samples in thick capillaries while the

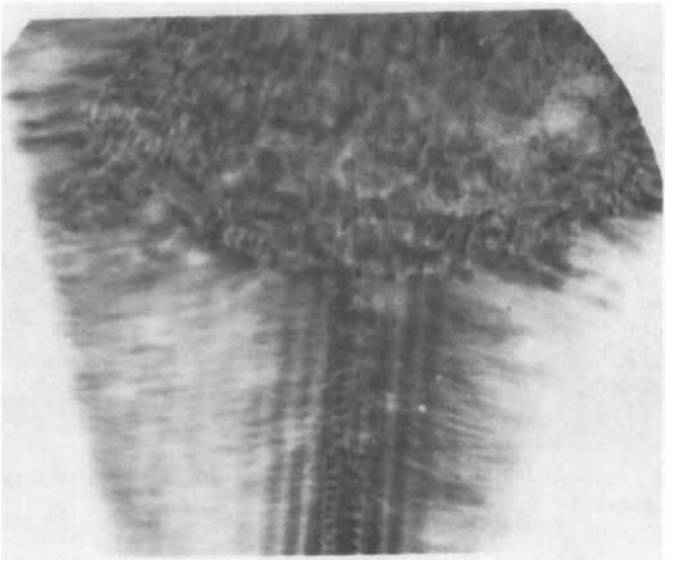

FIGURE 4 OM of a sample in a conic capillary showing the region of changement of texture (magnification 125 ×).

texture of the lower part is typical for samples in thin capillaries. The discontinuity appears for thicknesses around 1.5–1.9 mm and is not necessarily connected with the different orientation induced by the interface with the air, since the typical texture for thick samples appear also when XD has equatorial orientation. This discontinuity is connected with the fact that the wall layers meet at the centre of the sample, resulting a totally oriented sample by surface effects.

Samples in thin capillaries (typically 0.7 mm) show by OM colored lines parallel to the capillary axis, that are sometimes disturbed by a point disclination. An example is shown in Figure 5; these singular points are rather similar to the so-called umbilics.[10]

The analysis of the compromise between surface and magnetic orientation (Freederickz transition) was made by XD using the fact that surface orientation results in an equatorial diffraction that disappears with magnetic orientation when $\vec{H}$ is in the equator direction ($G_\perp$). The geometry is sketched in Figure 1b; in this case we have a mixture of splay and bend and therefore it is not possible to obtain a defined elastic constant, but only an average value, admitting that $k_1 \cong k_3 \cong k$.

Initially the conic capillary was used with constant field, but it was concluded that the collective effect of wall orientation in the thinner

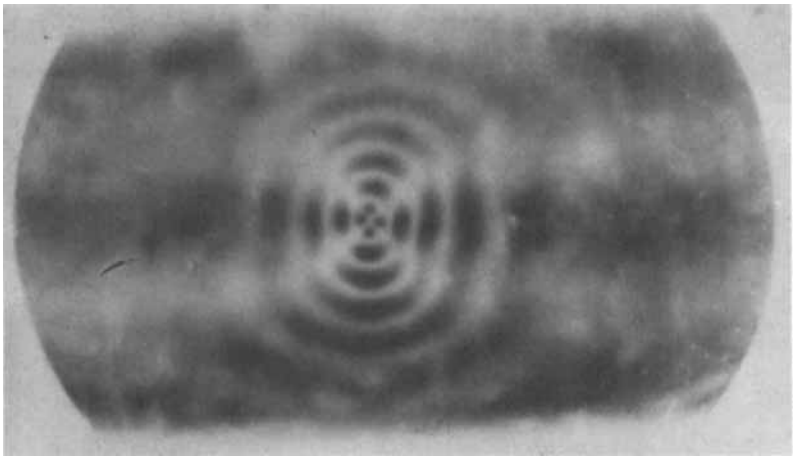

FIGURE 5 Point disclination observed by OM in sample in 0.7 mm thick capillary (magnification 125 ×).

part of the sample influenced strongly the behaviour of the orientation in the thicker part, making the analysis in terms of a Freederickz transition extremely difficult.

Measurements were then performed in several Na glass capillaries of unique thickness, varying the applied field of the electromagnet. It was then possible to determine a critical field of (200 ± 50) G for a thickness of 0.5 mm. For a 0.3 mm capillary the maximum field (800 G) was below the critical field. Admitting for the critical field the behavior expected from the continuum theory for the Freederickz transition, these results can be used to estimate the elastic constant, using for the magnetic anisotropy the estimated[11] value of 10^{-8} emu/cm^3. It results $k = (1 \pm 0.5)10^{-7}$ dynes, from 0.5 mm thickness; $k > 6.10^{-7}$ dynes, from 0.3 mm thickness.

Although these results are not completely conclusive and the Freederickz transition shall be studied also by traditional optical methods, they seem to indicate a complex behavior, connected with different levels of anchoring at the surface. The capillary thickness dependence of k must be due to variations in the strength of surface anchorage; weaker surface anchorage gives rise to smaller critical fields and lower apparent k values.

There is therefore evidence, both from the results of the Freedericks transition with capillaries of unique thickness and the failed attempt with the conic capillary, as well as from the observed discontinuity by OM, that the strength of surface anchorage depends on the boundary

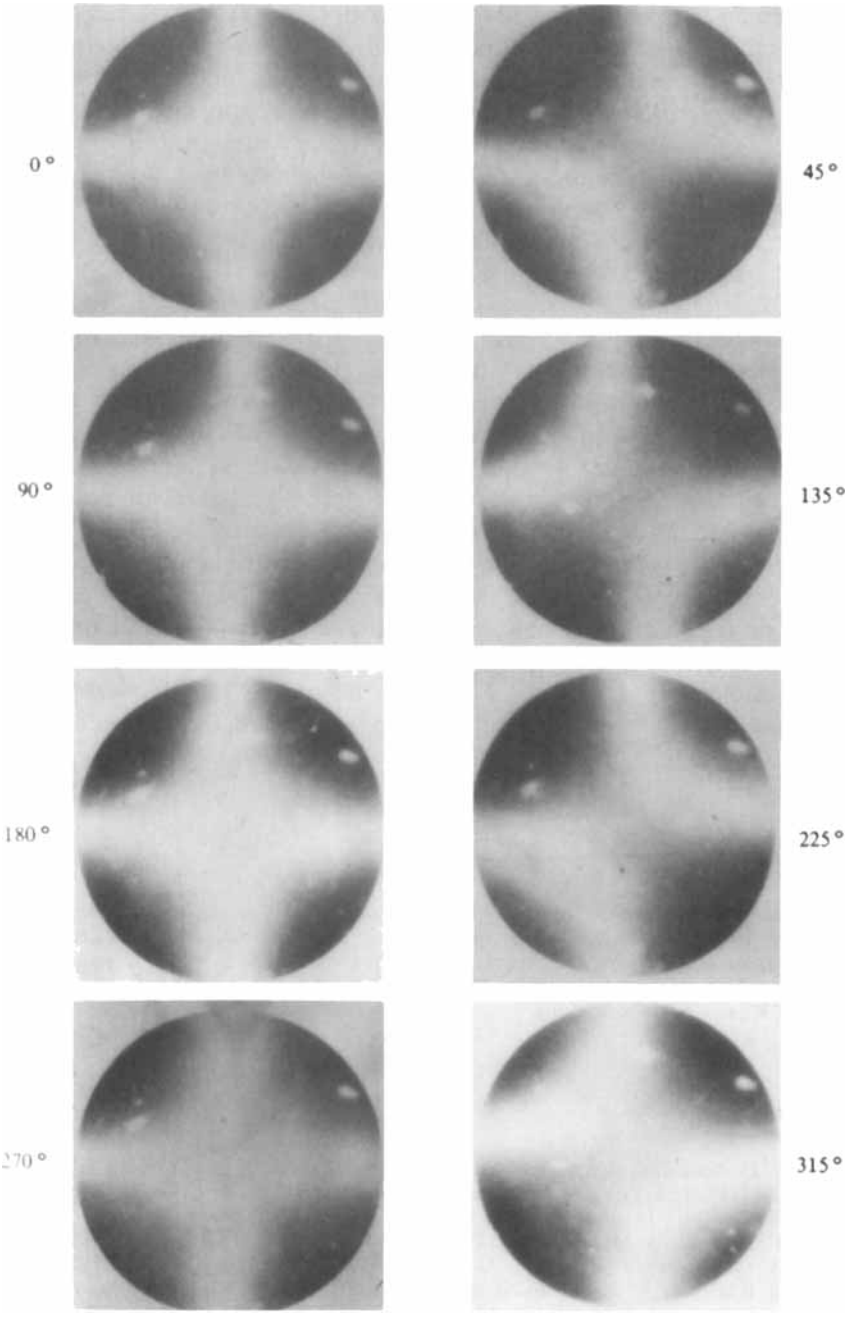

FIGURE 6 Weak biaxiality evidenced by successive 45° turns of the sample.

condition at the other end of the wall layer. It has therefore a collective character and does not depend entirely on the characteristics of the interaction between the wall and the nearest micelles.

Some attention has been paid in this study also to the orientation times of the samples in magnetic fields. For 0.7 mm samples in a 2.5 KG magnet, orientation started after 2 minutes and was almost complete after 3 hours, while the disorientation process was almost complete after 5 hours, as visualized by OM. For 2 mm thick samples in the same field, orientation started after 2 hours and was almost complete after 24 hours, while the disorientation process could take several days. Flat samples 0.3 mm thick under influence of wall orientation required one day to acquire the pseudo–isotropic orientation. These relaxation times are much larger than those for thermotropic nematics and indicate rather large rotational viscosities (of the order of 1 poise), in spite of the high fluidity of these samples.

Textures observed by OM in flat samples are typical of nematic lyomesophases. Analysed by OM, the sample has positive axiality, but shows also a weak biaxiality, that cannot be attributed to the glass plates. The weak biaxiality, shown in Figure 6, appears mostly at the central region of the sample; near the borders of the flat capillary the figure is typical of slight misalignment of the optical axis in relation to the microscope axis. This effect may be of the same type as the so-called[12] apparent biaxiality due to oriented defects in lamellar liquid crystals.

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