

Formation Process of CdS Nanorods via Solvothermal Route

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Received January 6, 2000. Revised Manuscript Received July 27, 2000

The formation process of CdS nanorods prepared by the reaction of thiourea and cadmium nitrate in ethylenediamine was investigated in detail by X-ray powder diffraction, transmission electron microscopy, selected-area electron diffraction, and IR techniques. An accordion-like folding process was proposed to account for the formation of CdS nanorods. Further studies indicate that the dissociation of ethylenediamine molecule adsorbed on the surface of CdS results in the formation of CdS nanorods. The obtained CdS single-crystal nanorods showed an abnormal electron diffraction that was explained by the double diffraction of the incident electron inside the sample. The result from electron diffraction confirmed that CdS nanorods grew along *c* axis.

Introduction

With crystal size decreasing, the energy band of semiconductor nanocrystallites evolves from sequential to discrete energy levels, which causes semiconductor nanocrystallites display optical, electronic and structural properties to be different from those of bulk phase and isolated atoms.¹ In recent years, the morphology effect of semiconductor nanocrystallites on their physical properties has aroused extensive attention,² so that the syntheses of semiconductor nanowires, nanorods, or fibers have been the focus of current researches.^{3,4–14}

Since many fundamental properties of semiconductor materials have been expressed as a function of size and shape, controlling the size and shape of semiconductor nanocrystallites would provide opportunities of tailoring properties of materials and offer possibilities for observing interesting and useful physical phenomena.¹⁵ Therefore, the engineering of materials in nanometer-scale has attracted much attention in optics, electronics, magnetics, catalysis, and ceramics.¹⁶

To control the size and shape of nanocrystallites, all kinds of templates, such as liquid crystals, self-assembled monolayers (SAMs), polymers, or porous aluminum oxide, usually were used. For instance, Braun and co-workers synthesized CdS nanocomposites within a liquid-crystalline hexagonal mesophase formed by nonionic organic amphiphiles and water.⁴ Sailor's group and Martin established a new technique to fabricate II–VI semiconductor fibers by electrochemically depositing the semiconductor directly into the pores of an alumina nanoporous membrane.⁵ Subsequently, Moskovits successfully applied a similar technique to fabricate CdS nanowires.⁶ One-dimensional (1-D) GaN nanowires were synthesized in a novel template, carbon nanotubules, which was reported by Fan.⁷

Recently, 1-D nanostructure materials were synthesized without a template. Alivisato's group synthesized

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the elongated CdSe nanocrystallites by injecting a solution of dimethylcadmium and selenium in tributylphosphine into trioctylphosphine oxide (TOPO) at 340 °C and subsequently heating to 280 °C.^{8,9} Buhro's group successfully prepared 1-D crystalline III–V nanofibers by conducting a simple organometallic reaction in hydrocarbon solvents at low temperature. Meanwhile, they proposed a solution–liquid–solid (SLS) mechanism to explain the growth of the fibers.¹⁰

In the past several years, our group has been devoted to the syntheses of semiconductor nanowires via solvothermal processes.^{11–14} Wang obtained selenides nanowires at room temperature through the reaction of metal chlorides, KBH_4 , and Se powders.¹¹ Meanwhile CdE (E = S, Se, Te) nanorods were synthesized via simple solvothermal reactions.^{13,14} It was interesting to note that all of these syntheses were conducted in ethylenediamine (en). If en was replaced by other organic solvents, CdS nanorods were not observed in the products.¹⁵ So, further studies on the formation process of CdS nanorods in en are important to design a possible pathway to other 1-D material nanorods. In this paper, we aim to study this formation process of 1-D CdS in en and the role that en played in this process.

In this paper, we illustrated the detailed formation process of CdS nanorods by using X-ray powder diffraction (XRD), transmission electron microscope (TEM), selected-area electron diffraction (SAED), and IR techniques. The CdS nanorods were found to be formed through an accordion-like folding process that was caused by the dissociation of the en molecules adsorbed on the surface of CdS. The typical electron diffraction of CdS single-crystal nanorods was successfully explained by the double diffraction of the incident electron inside the sample. The analysis of electron diffraction revealed that CdS nanorods grew along the *c* axis.

Experimental Section

All of the reactants and solvents are analytical-grade and are used without any further purification. In a typical procedure, an appropriate amount of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_2\text{-CSNH}_2$ (molar ratio, 1:3) was added into a Teflon-lined stainless steel autoclave which had been filled with ethylenediamine to 80% of its capacity. Samples a, b, c, and d were taken out of the furnace after the reaction had been carried out at 120 °C for 1, 1.5, 2.5, and 3.5 h, respectively. Then, they were cooled to room temperature immediately. The precipitates were filtered. Parts of every sample were sent for the characterization with IR without any post-treatment. The others of every sample were washed several times with distilled H_2O and absolute ethanol to remove the excessive thiourea and other byproducts. Finally, they were dried in a vacuum at 70 °C for 0.5 h. The powders were collected for the characterization with XRD, TEM, scanning electron microscopy (SEM), SAED, and X-ray photoelectron spectra (XPS).

XRD patterns were obtained on a Japan Rigaku D/Max- γ A rotation anode X-ray diffractometer equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), employing a scanning rate of $0.02^\circ \text{ s}^{-1}$ in the 2θ range from 10° to 70° . TEM and SAED photographs were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The samples for these measurements were dispersed in absolute ethanol by being vibrated in the ultrasonic pool. Then, the solutions were dropped onto Cu grids coated with amorphous carbon films. SEM photographs were taken from a Hitachi X-650 scanning electron microanalyzer. XPS were recorded on a VEGSCALAB MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg- $\text{K}\alpha$ radia-

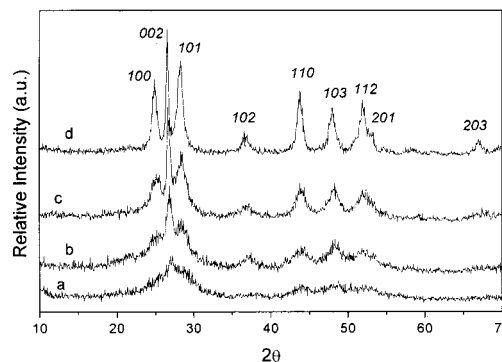


Figure 1. XRD patterns evolution during CdS nanorods formation: samples (a) a, (b) b, (c) c, and (d) d.

tion as the excitation source. IR spectrum was recorded on a Bruker Vector-22 FT-IR spectrometer scanning from 4000 to 400 cm^{-1} at room temperature. The samples were ground with KBr crystal, and the mixture of them was pressed into a flake for IR measurement.

Results and Discussions

The XRD patterns at the whole process showed that the crystallinities of the samples were continuously improved with the reaction time being prolonged. Furthermore, a preferential orientation and a rodlike shape were observed in the later samples.

The XRD pattern (Figure 1a) of sample a showed that the majority of the products were poorly crystallized. XPS were used to determine the composition of this sample. The binding energies of $\text{Cd}3d_5$ at 404.75 eV and $\text{S}2p$ at 161.11 eV revealed that this sample could be identified as CdS.¹⁶ The atom ratio of Cd/S calculated from the peak areas of $\text{Cd}3d_5$ and $\text{S}2p$ was 46.2:53.8, which is in agreement with the stoichiometry of CdS. When the reaction time was prolonged, the crystallinity of sample b was obviously improved, as shown in Figure 1b. Although the diffraction peaks of (100), (002), and (101) could not be well distinguished, it was noted that the diffraction peak of (002) was stronger than expected. If the reaction lasted for a longer time, the diffraction peak of (002) in sample c became both stronger and narrower than those of others, as shown in Figure 1c. This unusual diffraction peak of (002) indicates a preferential orientation along the *c* axis and a rodlike shape.^{12,13} The preferential orientation was confirmed by a rocking curve, and the rodlike shape was confirmed by TEM photographs that will be discussed later. After the reagents reacted for 3.5 h, this characteristic of the diffraction peak of (002) was kept in Figure 1d, which implies the preferential orientation and the rodlike shape are unchanged in sample d. However, its crystallinity was higher than that of the former. The XRD pattern of sample d was indexed as a pure hexagonal phase with cell constants $a = 4.12 \text{ \AA}$ and $c = 6.68 \text{ \AA}$, which are very close to the values in the literature (JSPDS Card, File No. 41-1049).

TEM photographs showed that there was an accordion-like folding process in the morphology evolution of the samples. When observed with electron microscopy, sample a displayed a lamellar shape, as shown in Figure 2a. There were many folds on the lamellae. The SAED pattern (Figure 2a inset) consisted of several diffused diffraction rings, which indicates that sample

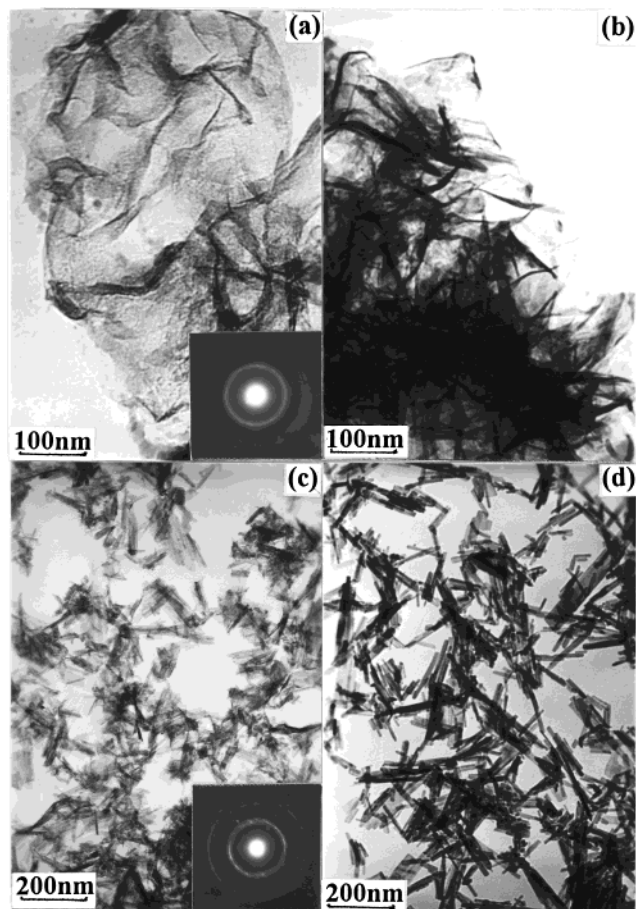


Figure 2. TEM photographs and SAED patterns during CdS nanorods formation: samples (a) a, (b) b, (c) c, and (d) d.

a is poorly crystallized. This result is consistent with that from its XRD pattern. TEM photograph (Figure 2b) of sample b revealed that the number of the folds increased and that these folds spontaneously agglomerated together. It seems that the shrink of the lamellae leads to both the increase of the folds and the agglomeration of the folds. There was an interesting change in the morphology of sample c: the previously agglomerated folds broke into needlelike fragments, as shown in Figure 2c, which is very critical in the formation process of CdS nanorods. On its SAED pattern, the electron diffraction of (002) showed a preferential orientation, which coincides with the result from its XRD pattern. Due to its higher crystallinity and larger size, sample d, which is composed of short nanorods and is 12–17 nm wide and 40–160 nm long, can be observed more clearly.

According to these results, the formation of the obtained nanorods can be divided into several steps. First, cadmium nitrate and thiourea reacted to produce the lamellar CdS with many folds on it. After that, the folds on the lamellae agglomerated together. Then, these folds broke into needlelike fragments. Finally, these needles grew to well-crystallized nanorods. This transition process is very interesting and is very different from the formation process of III–V nanofibers and M_2S_3 ($M = \text{Sb, Bi}$) nanorods.^{10,17}

The similar process that rods were formed through the folding of lamella in a surfactant mesophase has

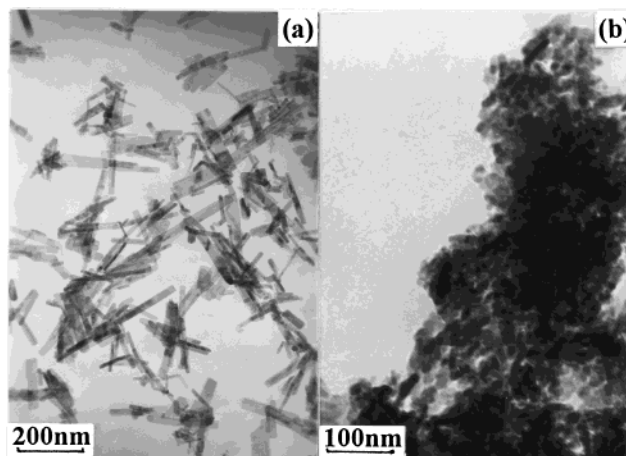


Figure 3. TEM photographs of products obtained by placing sample a (a) with no treatment and (b) without en molecule into absolute ethanol at 120 °C for 10 h.

been reported by Yada et al.¹⁸ They found that the folding of aluminum-based flexible layers produced various precursors which then grew to versatile morphologies including the rodlike shape.

It was believed that the en molecules adsorbed on the samples determined this morphology transition and the en molecules in the solution were not relevant to this transition process. To confirm this conclusion, sample a without any post-treatment was kept in absolute ethanol at 120 °C for 10 h. The obtained products were composed of CdS needles completely, as shown in Figure 3a. However, if the en molecules adsorbed on sample a were removed by washing sample a several times with distilled H_2O , most of the products prepared under the same condition were uniform spherical particles, as shown in Figure 3b. The very small amount of nanorods can be attributed to the remnant en molecules on sample a due to incomplete washing. A comparison of the results of two experiments demonstrates that the transition process depends on the en molecules adsorbed in the initial sample, which coincides with the above conclusion. Meanwhile, this result implies that this transition process can also be conducted in other solvents, as long as the en molecule has adsorbed on the initial sample.

Therefore, to further ascertain the function of the en molecules adsorbed on the surface of CdS in this complicated transition of the morphology, IR spectra of the samples obtained at different times were measured without any post-treatment.

The starting solution was evaporated in a vacuum at room temperature to several drops. Then, IR spectrum was measured at room temperature by dropping the solution on a KBr window. To conveniently compare with literature values, the values of absorption peaks from 2000 to 500 cm^{-1} were listed in Table 1. For the sake of clarity, the absorption peaks at 1384.6 and 821 cm^{-1} , which can be attributed to the vibration of NO_3^- anion ion, were omitted from Table 1. By contrast to the literature,¹⁹ the IR spectrum of the starting solution was similar to that of $[Cd(en)_3]^{2+}$. It implies that the

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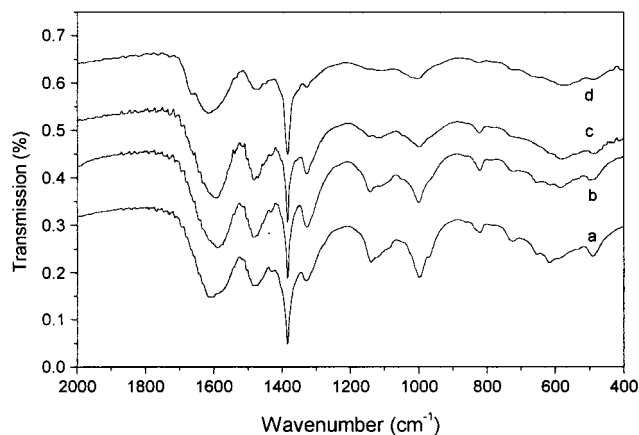


Figure 4. IR spectra of CdS powders during nanorods formation: samples (a) a, (b) b, (c) c, and (d) d.

Table 1. Infrared Absorption Frequencies^a (cm⁻¹) of the Samples from 2000 to 500 cm⁻¹

starting solution	Cd(en) ₃ Cl ₂ ²²	en adsorbed on CdS	Cd(en)Cl ₂ ^{24,25}
1666.5m	1675m		
1599.3s	1604s	1614s	1614s
1579.1s	1568s		
	1500m		
1482.4m	1478m	1480m	1481m
1464.1m			
1455.8m	1455m		
1398.5s	1397m		
1334.7s	1338m	1328m	1334m
1280.9m	1282m		
1136.9m	1134s	1140m	1097m
1027s	1028s		
1008vs	998vs	1000m	1014m
968.4vs	967vs		
863.9m	869m		
709.3m			
629.1m	622s		
		572m	540s

^a Key: vs, very strong; s, strong; m, middle. Weak peaks were omitted for the table.

en molecules in the starting solution use a gauche conformation to chelate with Cd²⁺ just like that in [Cd(en)₃]²⁺.²⁰ Although there was thiourea in the solution, the coordination ability of thiourea is much smaller than that of an en molecule.²¹ Therefore, the complex between thiourea and Cd²⁺ ion was not observed in the IR spectra.

The IR spectra of the samples obtained at the different times were similar to each other (Figure 4), but they were much simpler than that of the starting solution. Since CdS has no absorption peaks in the range of the middle infrared region and these IR spectra cannot be identified as pure en molecule,²² they must be caused by the en molecules adsorbed on the surface of CdS. It was found that these absorption peaks were close to those of Cd(en)Cl₂ (Table 1) in which an en molecule uses a trans conformation (Chart 1) to bridge adjacent cadmium ions.^{23,24} This result indicates that the en molecules probably use the trans conformation to coordinate with Cd²⁺ on the surface of CdS, which can be attributed to the sulfur bonded with Cd²⁺ that impeded

Chart 1. Trans conformation of en molecule.

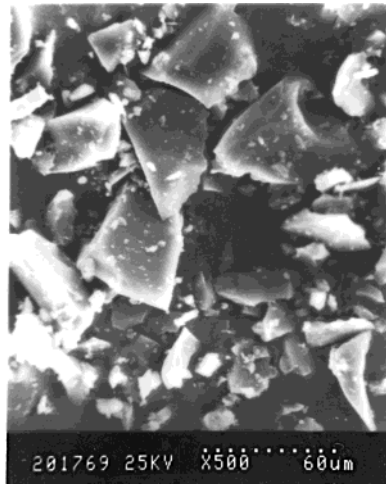
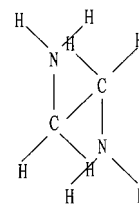


Figure 5. SEM photograph of the products obtained in *o*-phenanthroline at 210 °C for 36 h.

the formation of the chelate structure between en molecule and Cd²⁺ on the surface of CdS.

The trans conformation of the en molecules adsorbed on the surface of CdS is important to the formation of CdS nanorods through this process. To certify this conclusion, *o*-phenanthroline was chosen as the solvent to prepare CdS powders by the same reaction at 210 °C for 36 h, since it merely forms the chelate structure with Cd²⁺ and its chelate ability is close to that of ethylenediamine.²¹ As shown in Figure 5, only irregularly shape particles were observed in the product. This result demonstrates the importance of the conformation of the en molecule from the back.

Although the IR spectra of the samples obtained at different times were similar to each other, it was noted that the intensity of absorption peaks of the en molecules adsorbed on the surface of CdS gradually decreased with regard to the adsorption peak of NO₃⁻ at 1384.6 cm⁻¹ (Figure 4). This indicates that the en molecules dissociate from the surface of CdS nanocrystallites during the morphology transition. It is believed that the high temperature weakens the interaction between the en molecule and Cd²⁺ on the surface of CdS, which leads to this dissociation. This conclusion has been confirmed by our experiments. When the obtained samples without any post-treatments were heated in a vacuum at 70 °C for 1 h, the absorption peaks that belonged to the en molecules adsorbed on the surface of CdS greatly decreased in the intensity. However, there was no shift in the position of IR peaks. This indicates that the interaction between the en molecule and Cd²⁺ on the surface of CdS is destroyed.

If the dissociation of the en molecules adsorbed on the surface of CdS is restrained, the morphology transition will slow or even stop. For example, when sample a without any post-treatment was put into benzene at 120

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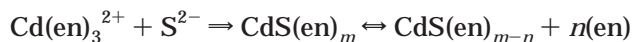
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°C for 10 h, the products kept almost the original morphology. This can be attributed to the fact that the low solubility of an en molecule in benzene limits the dissociation of these molecules. The result confirmed that the dissociation of the en molecules adsorbed on the surface of CdS lead to the morphology transition of CdS. This result also indicates that the dissociation of an en molecule in apolar solvent is much slower than one in polar solvent. In other words, the physicochemical properties of solvents have a great influence on the dissociation of the en molecules from CdS.

Associating all of these results, the whole process can be expressed as follows:



First, Cd^{2+} ion coordinated with en molecule to form Cd(en)_3^{2+} .¹⁹ Thiourea decomposed to produce S^{2-} at low temperature in the base environment.²⁵ Then, the reaction between Cd(en)_3^{2+} and S^{2-} produced CdS powder with its surface-adsorbed en molecule. Meanwhile, the conformation of the en molecule coordinated with Cd^{2+} changed from the gauche to the trans conformation. However, the interaction between the en molecules and Cd^{2+} on the surface of CdS was weak when the en molecule was in the trans conformation. Therefore, this structure was destroyed at high temperatures. This dissociation of the en molecules from the surface of CdS resulted in the evolution process of the morphology. In fact, the en molecule in the trans conformation acted as an intermediate.

The size of the CdS nanorods synthesized in ethylenediamine increases with the increase of reaction time or temperature, and the crystallinity is also further improved. Figure 6 presents a typical CdS nanorod 10 μm in length and 90 nm in width. Its SAED pattern shows that it is a well-developed single crystal (Figure 6b) with its growth direction along the c axis. It was found that the forbidden diffraction spot corresponding to (001) appeared in the diffraction pattern, which was not observed in all of the XRD patterns. This anomaly arises from the double diffraction of the incident electron whose scattering is much heavier than that assumed in the kinematical theory.²⁶ The forbidden diffraction spots which result from the double-diffraction process can be obtained by translating the primary diffraction

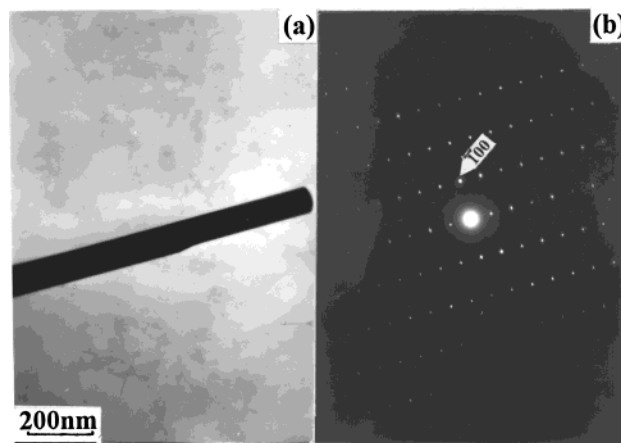


Figure 6. Typical CdS nanorods prepared in en at 250 °C for 12 h. (a) TEM photograph of CdS nanorods. (b) SAED pattern carried on part a in a [010] zone.

pattern, without rotation, so that its origin coincides successively with all of the strong spots of the primary pattern. Meanwhile, the unit cell of the hexagonal-phase CdS is a nonprimitive unit cell that provides the

necessary condition for the occurrence of the truly forbidden reflection. Therefore, the double-diffraction effect leads to the occurrence of the truly forbidden reflections. In addition, some striations nearly perpendicular to the growth direction can often be observed in the products, which is caused by stacking faults.²⁷

Conclusion

We investigated in detail the formation process of CdS nanorods in a solvothermal route. With the increasing crystallinity of CdS powders, an accordion-like folding process was observed in the evolution of the morphology. The results showed that this evolution process was caused by the dissociation of the en molecules adsorbed on the surface of CdS. This dissociation can be attributed to the fact that the interaction between the en molecules and Cd^{2+} on the surface of CdS is weakened at high temperatures. The double diffraction of the incident electron was used to explain the abnormal electron diffraction of CdS single-crystal nanorods.

Acknowledgment. The work is supported by the Chinese National Foundation of Natural Science Research and Anhui Provincial Foundation of Natural Science. We thank Prof. K. S. Chen and Mr. G. H. Chen for the beneficial discussion.

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