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Absorption phenomena in organic thin films for solar cell applications investigated by photothermal deflection spectroscopy

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A high sensitive approach is presented to detect in particular the low level absorption features in pure and blended organic semiconductor films, revealing a.o. defect induced sub gap absorption and new interactions between the materials. Because sub bandgap absorption features are typically characterized by very low absorption coefficients, it is not possible to resolve them using common transmission and reflection measurements. Therefore the very sensitive and ground state spectroscopic technique of Photothermal Deflection Spectroscopy (PDS) has been developed, and introduced to characterize thin films of MDMO-PPV and PCBM, as well as films of MDMO-PPV containing an increasing amount of PCBM ranging from 5 to 90% weight fraction. The measured spectra of MDMO-PPV are interpreted in terms of defect induced absorption phenomena. The spectral position of the observed transitions in PCBM have been determined and verified. The PDS-study on MDMO-PPV/PCBM blended films revealed for the first time interaction between the two materials in the ground state. To get more insight in the interaction mechanism between the constituting materials a systematic Transmission Electron Microscopy (TEM) study has been carried out to reveal the morphology of the films. The obtained TEM-results on nanomorphology of the blended films show clear correlations with the PDS-results.

1. Introduction

The increasing world energy consumption and the environment related, and the globally arranged constraints concerning this matter, have put renewable energy sources in an increasingly important perspective. In this field, solar energy conversion will play a major role in the future, and thus many innovative ideas have been launched and developed in the recent past. One of the fields, which has experienced an enormous boost, is that of fully organic, so-called "bulk heterojunction" solar cells. A type of cell with an active layer, based on an electron donating material, interfacing an electron accepting moiety, creating a three-dimensional pn-junction and giving birth to a promising new concept of photovoltaic devices. This concept would indeed lead to cheap, low-weight and easy-to-produce solar cells. Although initial efficiencies reported are still low, a lot of progress has been made in recent years. A big step was made with the discovery of the influence of the morphology of the absorbing layer, taking the historical leap from $\eta = 0.9\%$ power conversion efficiency to a meritorious $\eta = 2.5\%$ [1]. The morphology of composite organic semiconductor films is extremely important for the charge generation and transport and thus the eventual performance of the solar cell. These effects were more profoundly investigated by Martens *et al.*, clearly demonstrating the importance of phase separated PCBM rich domains in a matrix, consisting mainly out of MDMO-PPV [2, 3]. This is an aspect of bulk heterojunction solar cells of which its significance will also be stressed in the work presented is this paper. Further optimisation of material combination and production procedures increased the efficiency up to $\eta = 3.5\%$ [4, 5]. Very recently, according to their press release, the important benchmark of $\eta = 5\%$ was reached by Siemens AG, making the bulk heterojunction a commercial viable alternative for inorganic solar cells [6].

As a bulk heterojunction, the combination of a p-conducting conjugated polymer, poly(2-methoxy-5-(3′, 7′-dimethyl-octyloxy))-p-phenylenevinylene

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(MDMO-PPV), and a strong electron acceptor, the soluble C_{60} derivative (6,6)-phenyl-C_{61}-butyric-acid (PCBM) has been most thoroughly investigated. Exhaustive optimisation lead to devices with power conversion efficiencies around $\eta = 3\%$, with an active layer of MDMO-PPV and PCBM in a 1:4 ratio, spin coated from a chlorobenzene solution [4]. The combination of conjugated polymers and C_{60} has been subject to many ground state and excited state spectroscopic studies in order to reveal the mechanism of photo-production of charge carriers [7, 8]. It was concluded that the materials show no interaction in their ground state, as the UV-Vis absorption spectrum of the composite films is a simple superposition of the spectra of the pure materials. As will be shown in the following, there are strong indications that these conclusions are premature and that indeed an interaction occurs. In the excited state, Photoluminescence (PL), Photo-induced Absorption Spectroscopy (PIA) and Light induced Electron Spin Resonance (LESR) have delivered sound proof that an ultra fast electron transfer reaction takes place from the excited conjugated polymer to the C_{60} molecule [7–10]. This process creates a mobile electron on the C_{60} moiety, leaving a highly delocalised polaronic species behind on the conjugated chain and opens the pathway for photo-induced current generation and thus for fully organic photovoltaic devices. More recently, experimental data demonstrated a similar ultra fast electron transfer (~40 fs) from excited MDMO-PPV onto PCBM, resulting in a quantum yield for charge generation of 100% [11]. Moreover, the resulting state is of metastable nature, so that an intimate mixing of both materials does not only enhance charge carriers generation, but also prevents recombination, detrimental for efficient photocurrent production [12].

This work presents an alternative approach to investigate the ground state absorption of pure organic semiconductors and their blends as used in organic photovoltaic devices, strongly focussing on sub gap absorption features and providing supplementary information on the DOS in the gap of both pure and mixed semiconductors. In this way, more insight can be obtained in the process of charge generation and recombination and charge carrier trapping by defect states. Because subbandgap absorption features are typically characterized by very low absorption coefficients, it is not possible to resolve them using common transmission/reflection measurements. Therefore the very sensitive and ground state spectroscopic technique of Photothermal Deflection Spectroscopy (PDS) has been used. The principles of the technique have been described earlier [13]. In the past, PDS has successfully been applied to directly measure the gap-state absorption in a-Si:H [14]. Recently, the technique has been used to detect sub gap absorption features in σ- and π-conjugated polymers [15–17]. Here, PDS is introduced to characterize thin films of MDMO-PPV and PCBM, as well as films of MDMO-PPV containing an increasing amount of PCBM ranging from 5 to 90% weight fraction. The spectra of the pure materials are interpreted in terms of a.o. vibronic progression, polaronic absorption, defect related absorption phenomena and $\pi \rightarrow \pi^*$ absorption. Surprisingly, the spectra of the compound films were not a simple superposition of the single component spectra, but additional transitions were detected, which would counter the wide spread conviction that no interaction occurs between MDMO-PPV and PCBM in their ground state.

To investigate whether there is a connection between the measured absorption spectra with PDS and the morphology of the layers, a systematic Transmission Electron Microscopy study (TEM) has been performed on MDMO-PPV films containing 5, 20, 50, 60, 70, 80 and 90% of PCBM weight fraction.

2. Experimental

2.1. Sample preparation

The conjugated polymer MDMO-PPV was synthesized via a precursor route described elsewhere[18]. PCBM was purchased from the laboratory of Prof. J. C. Hummelen, division of the Materials Science Center of the University of Groningen. These chemicals were not subjected to any purification prior to use. Sample preparation for as well PDS and TEM purposes, started from solutions based on chlorobenzene (p.a.) as a solvent. In this way solutions of 0.7% (w:v) of MDMO-PPV and 2% (w:v) of PCBM were prepared and stirred overnight. To obtain solutions with a fixed proportion of PCBM to MDMO-PPV, the proper amount of both chemicals was weighed and solubilized in order to obtain a 0.7% (w:v) solution, i.e. MDMO-PPV concentration, and stirred overnight. Films to be measured by PDS were prepared by drop casting the proper solution onto Corning 7056 quartz substrates (6 × 12 mm) in N_2-atmosphere (Mbraun glove box system). TEM-preparations were made by dipping a copper grid into the solution.

2.2. Photothermal Deflection Spectroscopy (PDS)

PDS is a very sensitive technique that measures $\alpha(E)$, based upon a local heating of the sample by absorption of light of a certain (sub-gap) wavelength. In this technique, a periodically intensity modulated monochromatic light beam is focussed on the sample (pump beam). The light of the pump beam can be absorbed by the sample, and converted into heat by non-radiative deexcitation. As a result, a periodic heating is created in the sample, generating a thermal wave that propagates into the sample and its surrounding medium. Since the index of refraction shows a temperature dependence, these thermal waves cause a periodic change in index of refraction in the sample as well as in the surrounding medium. Therefore, in PDS, the sample is immersed in a liquid, characterized by large changes in index of refraction with small changes in temperature (CCl_4, Fluorinert®). These changes are probed by a HeNe laser (probe beam), directed parallel to the sample and perpendicular to the pump beam, exactly near the surface, only probing the changes of index of refraction of the liquid. To measure the PDS-spectrum,

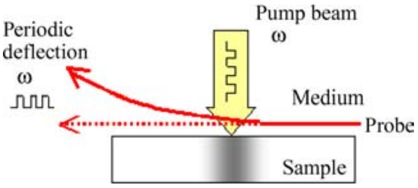

Figure 1 PDS working principle.

the drop casted films of the investigated materials on quartz were immersed in Fluorinert® FC75. The FC75 liquid was bubbled through with He, in order to remove all air traces. Subsequently, the sample was mounted in a N_2 atmosphere (glove box) in the cuvette which was sealed before measuring in air atmosphere. A simplified picture of the working principle is shown in Fig. 1. The obtained PDS-spectra need to be set on an absolute absorption coefficient scale, using standard transmission/reflection measurements in the high absorbing region as calibration data. This procedure includes the determination of $\alpha(E)$, using following formula:

$$\alpha(E) = -\frac{1}{d}\ln\left(\frac{T}{1-R}\right)$$

where T = transmission of the sample, R = reflectance of the sample, and d = thickness of the absorbing layer. It should be pointed out that in this formula scattering of the sample is neglected. Transmission and reflection of the samples was measured, using an Optronic OL750 spectrometer, equipped with a Si/Ge detector.

2.3. Transmission Electron Microscopy (TEM)

TEM analysis of the films on copper grid were made with a CM12 transmission electron microscope (Philips), equipped with a Energy Disperse X-ray (EDX) analysis system. Pictures of films up to 80% were completely amorphous and bright field images were taken. Films of 90% PCBM content showed interesting grains in the films, suggesting the presence of small PCBM crystallites. To exclude the possibility of contamination, several films were prepared and EDX-analysis was performed to determine the chemical composition of the repeatedly recurring grains. Bright field images of the films were recorded as well as Selected Area Diffraction patterns (SAD) of the crystallites. Corresponding dark field images have been taken and are shown in the following.

3. Results and discussion

3.1. PDS-results

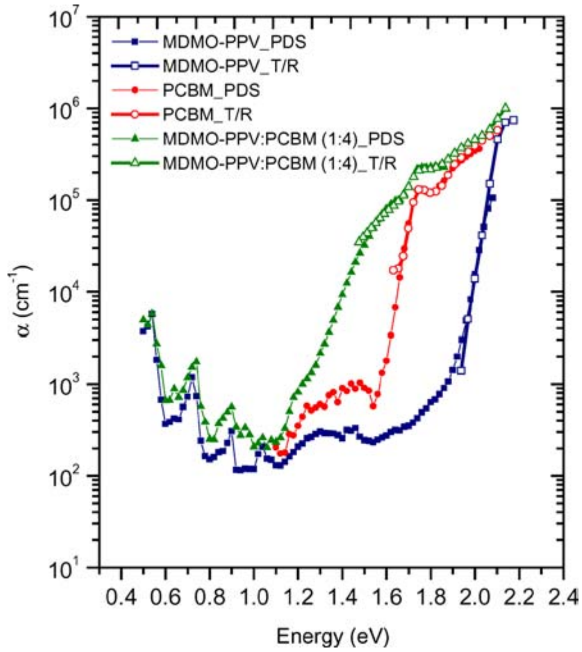

Figure 2 $\alpha(E)$ of drop cast film of MDMO-PPV (closed square: PDS-spectrum; open square: Transmission/Reflection), PCBM (closed circle: PDS-spectrum; open circle: Transmission/Reflection) and MDMO-PPV:PCBM (1:4) (closed triangle: PDS-spectrum; open square: Transmission/Reflection).

The PDS-spectra of MDMO-PPV, PCBM and MDMO-PPV:PCBM (1:4) are displayed in Fig. 2. The graph displays the dependence of the optical absorption coefficient α as a function energy E. All spectra are set on an absolute absorption coefficient scale by measuring separately the transmission/reflection of the PDS-films. The MDMO-PPV absorption can be divided into four regions: (1) 0.5–1.1 eV: multiphonon absorption, which is due to vibrational overtones of C-H stretching and bending vibrations. These absorption characteristics have been experimentally observed in previous PDS-studies of PPV [15, 19]. (2) 1.35 eV: this broad absorption is due to polaronic species present in the material, which originate from a residual doping of the polymer attributed to its synthesis and storage history. As the matter of fact, these polaronic species are characterized by a second broad absorption at 0.5 eV, with a comparable absorption coefficient. This band is indeed partly noticeable from 0.5 eV, on which the multiphonon absorption is superposed. (3) 1.5–1.9 eV: An absorption tail, due to transitions originating from the tail of localized states of the DOS distribution. Several experimental and theoretical studies have been made, which discuss the mechanism of photo-generation of free charge carriers in organic semiconductors [20–23]. As being a matter of great controversy, there are more and more indications that excitons are the primary photo-excitations in conjugated polymer. Subsequent to their formation, excitons exhibit a random walk within an energetically and spatially disordered array of hopping sites to eventually dissociate into pairs of free charge carriers at a charge transfer state, an impurity or defect. It however can pursue its random walk and bring about the excitation to be stronger localized on segments that belong to a deep tail of the DOS distribution. The observed tail in PDS-spectrum is interpreted as a direct measurement of this tail of localized states. (4) Gaussian $\pi \rightarrow \pi^*$ or band gap absorption, which also can be detected by common transmission measurements. The spectrum of PCBM consists of three main parts: (1) 1.1–1.54: Weak sub gap absorptions features of which the origin is not clear. (2) 1.54 and 1.74 eV: Orbitally forbidden HOMO-LUMO transition ($h_u \rightarrow t_{1u}$), analogous to the forbidden transition in C_{60} at approximately the same energy, which is due to a Herzberg-Teller distortion and characteristic for C_{60} and methanofullerenes [24]. The extra absorption at 1.54 is due to the transition from a triple degenerate LUMO in C_{60} to a double degenerate LUMO in methanofullerenes. An alternative possibility is that these transitions are originating from a spin and orbitally forbidden transition to the lowest triplet state[24, 25]. Triplet absorption spectra recorded by Bensasson *et al.* showed indeed absorption of C_{60} at 1.65 eV. The methanofullerenes they examined displayed the same absorption but blue shifted over 30 meV and splitted, giving rise to a shoulder at 1.51 eV. (3) >1.74 eV: Transitions from HOMO and HOMO-1 to higher excited states. The spectrum of composite film of MDMO-PPV:PCBM (1:4) is characterized by signatures of both materials. At low energy, the multiphonon absorption of MDMO-PPV is shown. At 1.74 eV, the characteristic absorption due to the presence of PCBM is clearly visible. A striking effect is the extra, broad absorption ranging from 1.1 to 1.68 eV, which is not present in the absorption spectrum of any of the pure materials. This suggests that both materials interact with each other to form a Charge Transfer Complex (CTC) which absorbs at lower energies. This assumption conflicts with the general believe that, based on UV-Vis absorption measurements, no interaction occurs between the two materials in the ground state. Increasing the sensitivity the measurement technique however, as being anticipated by PDS, revealed new spectral features of the 1:4 blend that clearly indicate the opposite. To investigate this effect more in detail, PDS-measurements have been made on films with different compositions, ranging from 5, 20, 50, 60, 70, 80 and 90% of PCBM weight fraction. The normalized PDS-spectra of these films are depicted in Fig. 3. From these measurements can be concluded that an as small PCBM content of 5% has a drastic effect on the spectrum. A broad absorption starts to appear between 1.1 and 1.68 eV, of which its significant growth is already concluded when the 20% content is reached. Increasing the PCBM content further only brings about a small blue shift of the spectrum, reaching its maximum at 60%. Our suggestion is that bringing in more PCBM in a matrix of MDMO-PPV creates a CTC, which absorbs light of wavelengths higher than the band gap of both organic semiconductors. The growth of this absorption goes on just as long the potential of creating a close interface between MDMO-PPV chains and PCBM molecules is possible. This border is determined by the percolation threshold and coincides with the observed completion of the growth of the CTC-absorption. A further addition of PCBM in MDMO-PPV, causes a strong growth of the PCBM absorption at 1.74 eV. It has been proven that an excess of PCBM in these measures can cause the system to phase separate, creating PCBM rich domains in a matrix of homogeneously mixed compound semiconductors [3]. This effect accounts for the increasingly pronounced PCBM absorption band in the spectra of the 60, 70, 80 and 90% films. To illustrate this, the spectra of these four films were plotted as an inset in Fig. 3.

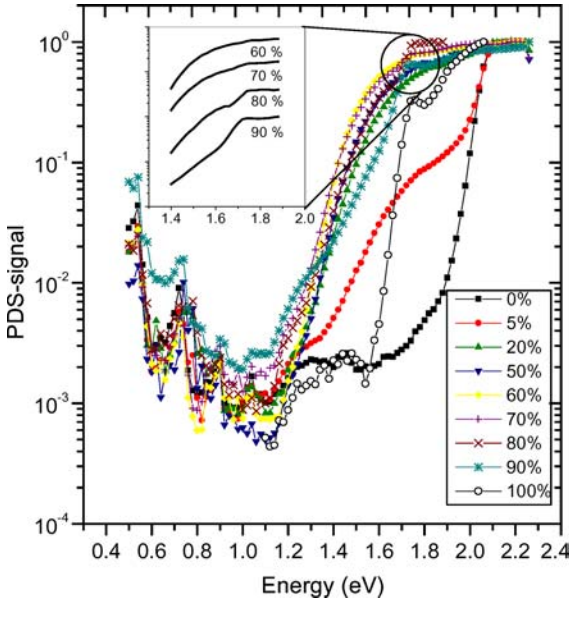

Figure 3 PDS-spectrum of a film of MDMO-PPV with a content of PCBM of 0% (square), 5% (closed circle), 20% (up triangle), 50% (down triangle), 60% (diamond), 70% (plus), 80% (cross), 90% (star) and a pure film of PCBM (open circle). Inset: PDS-spectrum from 1.4–1.9 eV of a film of MDMO-PPV with content of PCBM of 60, 70, 80 and 90%. The curves are shifted for clarity.

3.2. Influence of morphology

To relate eventual morphological matters to the observed changes in optical absorption as observed with PDS, a TEM study was performed on dipped films of MDMO-PPV, PCBM and compound films of 5, 20, 50, 60, 70, 80 and 90% of PCBM weight fraction. The images of these films are displayed in Fig. 4 and are taken at a magnification of 53000 times. A close look at the films of 5 to 50% of PCBM content reveal no interesting features i.e. only one homogeneous phase is imaged. Going over to 60% of PCBM, an ambiguous behaviour is observed, showing a monophasic system in one film, a small-scale phase separation in a second film (shown as inset of the image of the 60% PCBM film). This dual behaviour was also present in the 70% films (see also inset of the 70% PCBM film). Upon increasing the PCBM content up to 80%, the phase separation of the system is always present. The TEM picture shows dark, circular regions of PCBM rich domains in a matrix of a mixed MDMO-PPV:PCBM phase. It is clear that the phase separation is initiated, somewhere between 60 and 80% of PCBM content. The dipping method induces an irregular spreading of the starting solution over the copper grid, resulting in spots characterized by a different evaporation time and thickness. When the evaporation time is sufficiently long and the PCBM content is beyond a certain level, an observable phase separation will occur. It has to be concluded that there are two regimes in the evaluation of the nanomorphology of MDMO-PVV films ranging from 5 to 70% of PCBM content. At first, the formation of a partial percolated network of PCBM in a MDMO-PPV matrix sets in at 5% PCBM content, resulting in a full percolation already when the 20% PCBM content is reached. This effect visualized by the strongly growing absorption setting in at 1.1 eV as observed in the

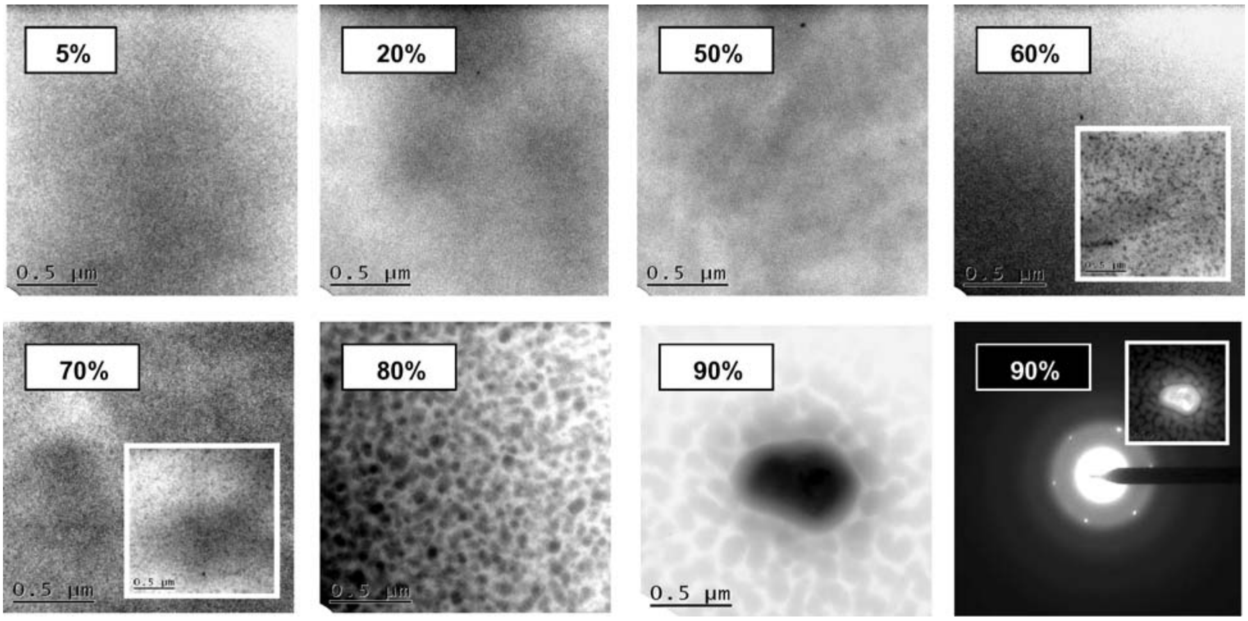

Figure 4 Left up to right down: bright field TEM images of MDMO-PPV films with a PCBM content of 5, 20, 50, 60, 70, 80 and 90%. The inset of the image of 60 and 70%: image of a different film with the same PCBM content. All images were taken at a magnification of 53000 times. *Right lower corner*: the Selected Area Diffraction pattern of the crystallite present in 90% film. The inset of the diffraction image is the corresponding dark field image of the crystallite.

PDS-spectra, an effect very similar to the process of strong photoluminescence quenching of a conjugated polymer when adding small amounts of PCBM [26]. TEM measurements revealed a phase separated system forming at a certain level of PCBM between 60 and 80%. As last composite film, the MDMO-PPV film with a 90% PCBM content is examined. The occurrence of three important phases is displayed in the TEM bright field image of the film. (1) Small pieces are present in the film, which have never been detected at the same magnification in the films of lower PCBM content, suggesting the formation of small PCBM crystallites, due to the high content of PCBM in the film. (2) Dark PCBM rich regions that have evolved from a circular shape to a network like shape (3) Matrix of a mixed phase of MDMO-PPV and PCBM. The Selected Area Diffraction (SAD) pattern of the lump was taken and displayed together with its corresponding dark field image in Fig. 4. Several films of MDMO-PPV with a 90% PCBM content were investigated in this way and the same three-component system was always visualized. To check whether contamination has occurred during the sample preparation procedure, EDX analysis has been performed on the present pieces to check their chemical composition. In any case, there was no trace of any unexpected elements, which confirms the supposition that indeed crystals of pure PCBM are formed. The measured diffraction patterns of the crystallites are being analysed to get a complete insight of the crystal structure of PCBM.

4. Conclusions

A novel spectroscopic approach was introduced to investigate thin films of pure and compound organic semiconductors. Photothermal deflection spectra of the pure MDMO-PPV films revealed low-level sub band gap absorption phenomena, which were explained in terms of vibrational signature, defect and disorder related absorption. The PCBM spectrum was determined successfully and compared with previous spectroscopic studies concerning the matter. The composite films exhibited a strong red shift of the optical absorption with respect to the pure materials indicating a significant interaction between MDMO-PPV and PCBM in the ground state, giving rise to a possible CTC. To see whether morphological aspects are the origin of the observed changes in optical absorption, a TEM study was performed and revealed a phase separation process setting in when the 60% PCBM level in MDMO-PPV was reached. Increasing the PCBM content further resulted in a more expressed phase seperation eventually leading to the formation of PCBM crystallites when reaching a MDMO-PPV film with 90% PCBM content.

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