Anti-Stokes Photoluminescence of Monolayer WS_2

Aurélie Pierret, Hans Tornatzky,* and Janina Maultzsch*

Anti-Stokes photoluminescence excitation of a WS_2 monolayer flake between 10 and 300 K is reported herein. Even with continuous-wave lasers at low power, the emission of the exciton at excitation 100 meV below its emission energy at room temperature is observed. A mechanism which involves the trions as the intermediate state is proposed, leading to an efficient up-conversion process. In addition, it is demonstrated that phonons are the source of the additional energy needed by the system. Overall, the results provide evidence that anti-Stokes luminescence in transition metal dichalcogenides is very efficient.

1. Introduction

Photoluminescence (PL) up-conversion is a phenomenon where light emission at energies higher than the excitation energy is observed. This, at first sight, astonishing observation is due to intrinsic energy transfer. PL up-conversion, sometimes called anti-Stokes photoluminescence (ASPL), has been observed in many semiconductor materials, such as II–VI and III–V compound nanomaterials,[1–7] in bulk semiconductors,[8–10] or in carbon nanotubes.[11] The excess energy can be provided by high-energy free carriers through an Auger process, by phonons, or by a second photon in a coherent or two-step process.[5] Two-photon absorption can be achieved through high-power excitation, typically provided by short laser pulses. However, low-power continuous-wave (cw) excitation can be sufficient for the other processes, if intermediate real states are involved.

ASPL can be an ingenious way of imaging samples by getting rid of blinding normal Stokes PL, in particular in biology,[11] and can be useful for laser cooling as energy is removed from the system.

2D layered materials are currently in the center of tremendous interest. Because these layers do not have dangling bonds at their planar interface, their interaction with their surrounding environment is drastically decreased. This is a fundamental difference to the 2D structures studied until now, such as quantum wells of conventional 3D semiconductors (II–VI and III–V compounds), and this gives rise to specific properties. For example, in semiconducting transition metal dichalcogenide (TMDC) monolayers (MLs), the exciton binding energy is on the order of several hundreds of meV, implying the observation of exciton emission at room temperature.[12,13] Depending on the doping level, the luminescence of charged excitons (trions) is observed at room temperature as well.[14]

Recently, PL up-conversion has been reported in one of the TMDCs, tungsten diselenide WS_2.[15,16] Jones et al.[15] report an efficient energy transfer from the trion to the exciton state by a double-resonant mechanism. Manca et al.[16] show ASPL of *A*-exciton excited states and *B*-exciton by exciting the *A*-exciton. This allows them to gain a deeper understanding into excitonic states and processes in WS_2. However, to have a more complete view of the process, ASPL has to be conducted on an excitation energy range covering more than the excitonic transition.

Here, we report efficient luminescence up-conversion on a WS_2 ML flake at room temperature and at 125 K. By carrying out temperature-, power-, and excitation energy-dependent PL experiments, we are able to draw a picture of the mechanism taking place, highlighting the role of real intermediate states. Our experiments suggest that the trion is the most important state in ASPL of WS_2.

2. Results and Discussions

Figure 1a shows PL spectra of a ML WS_2 flake at room temperature at different excitation energies. The spectrum in blue corresponds to usual above gap or Stokes excitation at 2.71 eV. It is composed of two bands, the *A*-exciton at 2.01 eV and the negatively charged trion (A^-) at 1.98 eV.[14] When lowering the excitation energy closer to resonance with the *A*-exciton, i.e., to 2.03 eV (still above the exciton energy, cyan line) or to 1.97 eV (slightly below the trion energy, green line), a similar spectrum is observed. More surprisingly, at 1.89 eV excitation (red line), more than 100 meV below the PL maximum energy, emission from *A* and A^- is still observable. The intensity, however, is more than three orders of magnitude weaker. We observe this effect for all intermediate excitation energies between 1.86 and 2.00 eV (not shown), with a similar spectral shape.

The apparent small red shift between the PL spectra excited at 2.03 and 1.89 eV is probably due to laser-induced doping of the

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Dr. A. Pierret,[+] H. Tornatzky, Prof. J. Maultzsch
Institut für Festkörperphysik
Technische Universität Berlin
Hardenbergstr. 36, 10623 Berlin, Germany
E-mail: aurelie.pierret@ens.fr; ht07@physik.tu-berlin.de

Prof. J. Maultzsch
Department Physik
Friedrich-Alexander-Universität Erlangen-Nürnberg
Staudtstr. 7, 91058 Erlangen, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/pssb.201900419.

[+]Present address: Laboratoire de Physique de l'Ecole Normale Supérieure, ENS, Université PSL, CNRS, Sorbonne Université, Université de Paris, 24 rue Lhomond, 75005 Paris, France

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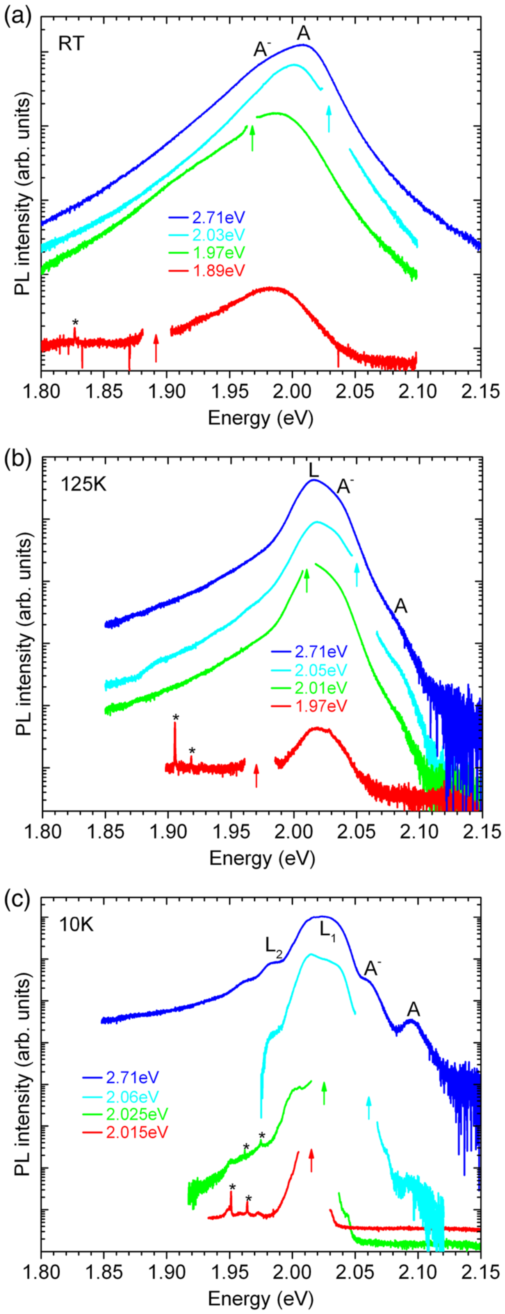

Figure 1. PL spectra at a) room temperature, b) 125 K, and c) 10 K, with different excitation energies in Stokes and anti-Stokes configuration. Spectra taken at different excitation energies are indicated with different colors. The arrows indicate the excitation energy, and stars the Si and WS_2 Raman peaks, when visible. A, A^-, and L denote the neutral exciton, the trion, and the localized states, respectively.

flakes with time, leading to a slightly modified ratio between exciton and trion intensity.[17] This is understandable considering our excitation power density of 200 μW μm^{-2}, higher than recommended in a previous study[17], but necessary with a low-transmittance triple-monochromator setup. During experiments, we were thus careful to illuminate the sample as shortly as possible.

Similar ASPL spectra were observed also on flakes directly exfoliated onto SiO_2. The advantage of using transferred flakes is that they are larger and less doped. The observed continuity of the PL signal intensity between the Stokes and the anti-Stokes side of the spectra means that the anti-Stokes process is as efficient as the Stokes one. This is similar to observations made on II–VI and III–V quantum dots and bulk GaN ASPL.[3–5,7,10]

At a lower temperature, spectral features become sharper and additional contributions are observed. At an intermediate temperature of 125 K (Figure 1b), the A and A^- peaks are better resolved, but localized states (marked as “L” in Figure 1b), probably originating from defects, become dominant. A possible biexciton contribution expected at 1.97 eV should be small[18] as our excitation power density is below 50 kW cm^{-2}. Similar to room temperature, luminescence is still observable when exciting below the exciton emission energy, with the intensity being several orders of magnitude lower (red spectrum in Figure 1b).

At 10 K, a different behavior is observed (Figure 1c). Whatever the excitation energy, the anti-Stokes side of the spectra is very weak or even vanishing. Only for an excitation around the trion energy, a weak peak of the neutral exciton can be seen with a low signal (cyan line). The signal measured on the high-energy onset of the spectra (few 10 meV above the laser energy) is probably the signal of the laser diffusion tail. With long integration time (5 min here), no significant signal can be measured at energies above these few tens of meV. This is very different from the observations at 125 and 300 K, and in contrast to the reported ASPL of WSe_2 in a previous study,[15] where excitation of the A^- trion leads to A-exciton emission even at 30 K (the excitation configuration of a previous study[15] corresponds to our measurements at 2.06 eV excitation at 10 K [cyan curve in Figure 1c], considering that our observation is the same at 10 and 30 K).

To confirm the increase in anti-Stokes efficiency with temperature shown in Figure 1, we recorded temperature-dependent PL at 2.33 eV (Stokes) and at 1.96 eV (anti-Stokes) excitation energy. **Figure 2**a shows the evolution of the integrated intensity (integration between 1.7 and 2.2 eV of the emission spectrum) of the luminescence as a function of temperature. For 1.96 eV excitation, spectra are interpolated between 1.93 and 1.97 eV because of the notch-filter rejection (see empty spaces in the spectra in Figure 1).

For Stokes excitation (green curve), the PL intensity decreases with increasing sample temperature. It has been reported that exciton luminescence of WS_2 is increasing with temperature because of its dark ground state.[19] But this is true only for the exciton with few nonradiative recombinations. Here the decrease with temperature is probably due to the activation of recombination paths due to the presence of defects. For anti-Stokes excitation (red curve), the effect is opposite: Between 80 and 300 K, the integrated intensity increases by more than four orders of magnitude. We note that, since the peaks are red-shifting with temperature by 80 meV, the 1.96 eV excitation at room temperature is almost in resonance with the trion. As we will see later (**Figure 3**b), an intensity decrease of two orders of magnitude is expected as a result of leaving the resonance condition by 80 meV. Here, however, the intensity drops by more than four orders of magnitude, implying an additional contribution. It can be a trion density increase and/or a phonon density increase. For the first possibility, this would be explained by the

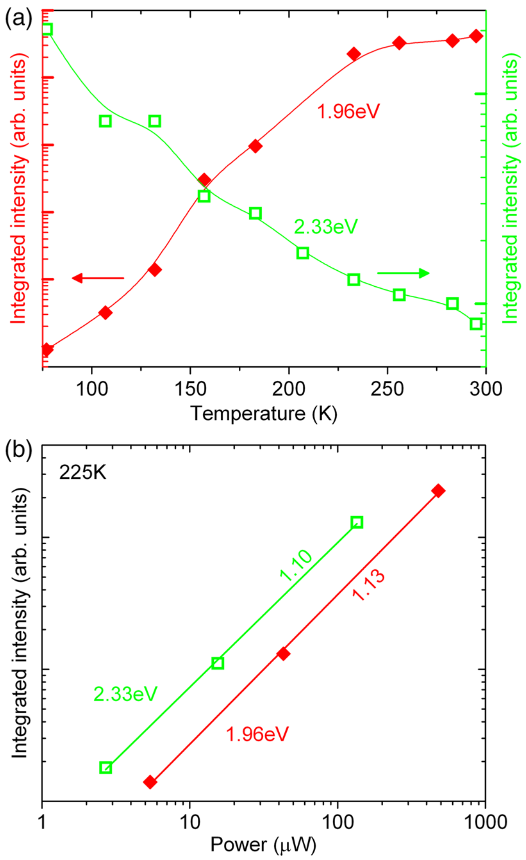

Figure 2. Integrated intensity of luminescence emission as a function of a) temperature and b) laser power at 225 K, with fixed excitation energies of 2.33 eV (green empty squares) and 1.96 eV (red diamonds), i.e., in Stokes and anti-Stokes configuration, respectively. In (a), lines are guides for the eye. In (b), lines result from the P^{α} fit with the slope α indicated.

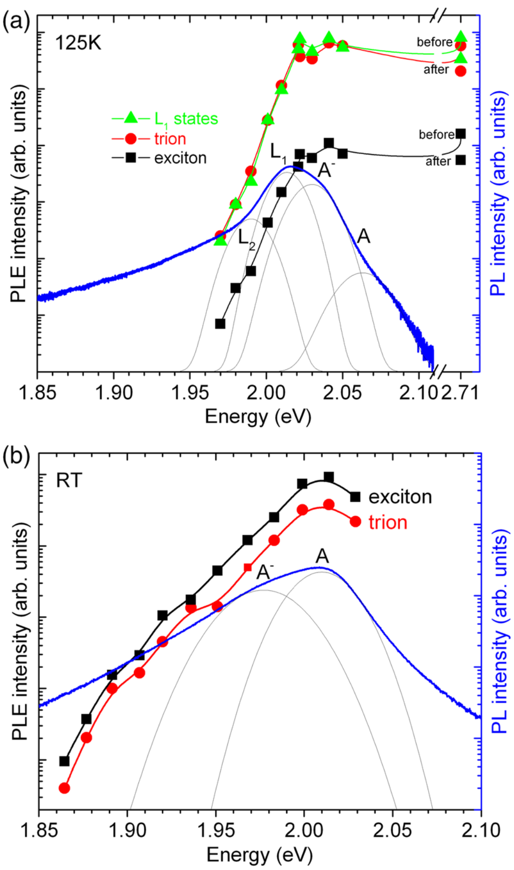

Figure 3. PLE spectra at a) 125 K and b) room temperature (symbols). The Stokes PL spectra (blue line) have been added for comparison, as well as its different components obtained by fitting (thin continuous lines). The lines connecting the symbols are guides for the eye.

fact that, our flake being substrate-induced doped, a relatively high density of populated donor or acceptor states is expected. At elevated temperatures, these states could ionize, leading to an increased free carrier concentration and thus an increased trion concentration. However, the intensity of the trion PL decreases with temperature increase, so this hypothesis is not consistent with our observations. Thus, the change in the ASPL intensity with temperature is more likely due to a change in phonon bath.

In semiconductor nanostructures, several processes are well known to lead to anti-Stokes PL:[5] Auger recombination, two-photon absorption, two-step photon excitation through an intermediate state, or a phonon-assisted process through an intermediate state. Their contributions can be distinguished by their excitation power dependence. Therefore, Figure 2b shows a logarithmic plot of the integrated intensity of the luminescence (between 1.7 and 2.2 eV) for different laser excitation powers (P) over two orders of magnitude (1–500 µV). The spectra have been recorded at 225 K in Stokes and anti-Stokes configurations with 2.33 and 1.96 eV excitation energy, respectively. The up-conversion process clearly follows a power law P^{α}, with $\alpha = 1$. In contrast, Auger recombination shows a cubic dependence on laser power and two-photon excitation a quadratic dependence. Only a phonon-assisted process with intermediate states should leave a linear intensity dependence with laser power, or a two-step process with photons and intermediate states, if the lifetime of the intermediate states is long. Therefore, we can exclude the first two processes as well as the involvement of intermediate states with short lifetimes. This is also consistent with the observation that only moderate excitation densities are needed. Consequently, we suggest that the observed anti-Stokes luminescence in WS_2 is generated by the excitation of an intermediate state. The required excess energy can be provided by a second photon or a phonon. To distinguish these two, the temperature-dependent measurements shown in Figure 2a are considered again: the increase in the integrated intensity for anti-Stokes excitation with increasing temperature strongly indicates a phonon-assisted process in WS_2 flakes.

Let us now turn to the determination of the involved intermediate states. First, as the process requires only low laser power, the involved intermediate states are likely to be real. These real intermediate-state transitions should give rise to resonance in photoluminescence excitation (PLE) experiments. We consequently recorded PLE spectra, i.e., we follow the evolution of the luminescence intensity at a given energy when tuning the excitation energy. This gives insights into the carrier relaxation path between absorption and emission lines. Figure 3 shows PLE spectra at a) 125 K and b) at room temperature. The data are obtained by fitting each emission spectrum obtained at different excitation energies by up to four Gaussians. The intensities of each relevant component of the fit (exciton, A^- trion, and localized L_1 states) are indicated by black squares, red dots, and green triangles, respectively. The anti-Stokes PL signal decreases with decreasing excitation energy, as already expected from the spectra in Figure 1 at 300 and 125 K. Here, only the exciton PLE spectrum is a pure anti-Stokes one, whereas for the trion and the localized states, only the lower energy part of the spectrum corresponds to anti-Stokes excitation conditions. For long excitation time and high laser power, according to the literature, the exciton line tends to disappear in favor of the trion and the localized L_1 and L_2 states lines,[17] which could explain the observed intensity decrease in the exciton transition. By comparing spectra taken before and after the series ("before" and "after" data points at 2.71 eV in Figure 3a), we observe only slight changes in the intensity of A, A^-, and L_1 peaks. These intensity drops are small compared with the observed changes under changing excitation energy and temperature, confirming that there is no flake degradation due to long exposure time. So, the decrease in the intensities, in particular of the exciton, has an intrinsic origin. Overall, the PLE spectra do not show any resonance effect but instead a continuous decrease in the intensity from a certain threshold.

At 125 K (Figure 3a), all three PLE spectra experience a common drop in intensity at roughly 2.02 eV, the energy of the trion. For the trion and the localized states, this threshold might be understandable because the excitation conditions are changing from Stokes to anti-Stokes configuration at this energy. In contrast, for the exciton, this change from ASPL to Stokes PL would be expected at a higher energy (2.06 eV, the exciton energy). Therefore, between 2.02 and 2.06 eV, there is an efficient up-conversion process. We thus propose that the trion is the intermediate state necessary for the anti-Stokes process to take place.

In addition, the decrease in the PLE intensity between 1.97 and 2.02 eV follows the line shape of the trion PL instead of the overall PL line shape including the localized states (blue line in Figure 3a). This further supports the dominant role of the trion as the intermediate state. An additional factor allowing an efficient up-conversion is that the energy difference between the trion and the exciton in WS_2 ML, 50 meV, coincides with the energy of the optical phonon modes at the Γ-point (A_1' and E' are both around 100 cm^{-1}, i.e., ≈50 meV).

At room temperature (Figure 3b), the observations are similar to 125 K. The PLE follows mainly the line shape of the trion, however, exhibits its maximum at the A-exciton peak (2.01 eV). We propose that this stems from the strong enhancement of the A-exciton emission (as shown in the included PL spectrum). The decrease in the PLE intensity toward lower energy is smaller at room temperature than at 125 K. It can be assigned to the broadening of the spectral features, an enhanced probability of the up-conversion due to the larger phonon bath, as well as a possible additional contribution of the localized states as intermediate states.

In summary, we have made the following experimental observations: 1) ASPL is observed with cw laser for the A-exciton, the A^- trion, as well as localized states (induced by defects); 2) the observation was done on transferred as well as directly exfoliated flakes; 3) the intensity of the ASPL is almost linear with excitation power; 4) ASPL is not observed below 30 K and is enhanced with increasing temperature; 5) no sharp threshold excitation energy is observed, below which ASPL cannot be detected; and 6) at 125 K, a decrease in the efficiency of the ASPL is observed when exciting below the trion state. At room temperature, the decrease is observed below the exciton state.

From these observations, we conclude that anti-Stokes luminescence takes place in WS_2 ML flakes through absorption of a photon, with energy corresponding to the trion energy, and phonons, see **Figure 4**. By exciting far below the exciton energy, we show additional contribution from the localized states, especially at room temperature.

Finally, we compare our results with the up-conversion in WSe_2 ML flake presented by Jones et al.[15] At 30 K, they observed a sharp resonance effect of the exciton emission when exciting at the energy of the trion. This seems comparable with our observations at 125 and at 300 K, the broader WS_2 emission in our case explaining the smoothing of the resonance conditions. The main difference to our results is their observation of ASPL at 30 K. Possibly, this can be explained by the phonon densities of the 50 meV phonons in WS_2 compared with 30 meV phonons in WSe_2 at a given temperature. At 30 K, the density of 50 meV phonons is three orders of magnitude smaller than the one of 30 meV phonons, leading to an even lower anti-Stokes PL in WS_2 than in WSe_2. Moreover the exciton to trion PL emission intensity ratio is more favorable for the exciton in WSe_2 than in WS_2[20,21] facilitating its observation after up-conversion. The high efficiency of the up-conversion process is underlined through the observation even at 30 K, where only a low density of phonons of few tens of meV (required for the up-conversion) are present.

We note that during writing of the manuscript, similar results have been reported for WS_2.[22] The authors observe anti-Stokes luminescence in an hBN-encapsulated sample at temperatures as low as 7 K using high excitation powers of up to 4 mW. Thereby, their findings in the high excitation power regime extend our observations at low powers.

In conclusion, we observed excitonic luminescence from a ML WS_2 flake excited several tens of meV below the exciton energy.

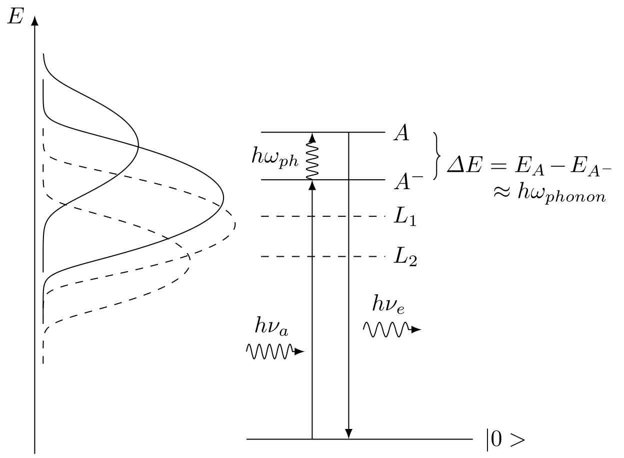

Figure 4. Sketch of the proposed model for ASPL in WS_2 ML. $h\nu_a$ and $h\nu_e$ are the absorbed and emitted photon energies, respectively, $h\omega_{ph}$ is the absorbed phonon energy, and E_A and E_{A^-} are the energies of the A-exciton and the A^- trion, respectively.

This anti-Stokes luminescence is composed of the entire excitonic spectrum (A-exciton and A^- trion), plus the localized states at low temperatures. The up-converted luminescence is strong, enhanced by temperature increase, and linearly dependent on excitation power. We propose that the photoluminesence up-conversion takes place via the trion as the intermediate state in a phonon-assisted process. Such a mechanism is rather unusual in semiconductor nanomaterials, as the intermediate states are typically defect states with long lifetime. Because the trion is the intermediate state, doping control through gating can modulate the intensity of the up-converted luminescence, which could be useful in future optoelectronics devices.

3. Experimental Section

Our samples are obtained by mechanical exfoliation of a synthetic WS_2 crystal (HQ Graphene) on a polymer (PDMS) stamp. The ML sheets are identified by optical contrast and then transferred onto a Si/SiO_2 substrate (90 nm SiO_2) using the dry transfer method presented in a previous study[23]. This method allows to obtain large ML flakes (several tens of µm) with reduced doping from the SiO_2 substrate, enabling the observation of A-exciton PL even under vacuum, rather than only the trion.[24,25] Optical contrast and Raman scattering experiments confirm the presence of the ML.

Micro-PL of WS_2 ML flakes was recorded either on a Horiba LabRAM HR setup or on a Dilor XY800 triple monochromator system. Several lasers were used for excitation energies in the range from 1.8 to 2.7 eV: an Ar^+/Kr^+ mixed-gas laser (457 and 514 nm), a frequency-doubled Nd:YVO laser (532 nm), a He–Ne laser (633 nm), and tunable dye lasers (LC6501 DCM Special—610–670 nm—and LC5900 Rhodamine 6G—605–630 nm). The laser beam was focused to a $\approx$1 µm spot using a 100× objective in confocal geometry. To avoid sample deterioration, the laser power was kept below 200 $\mu W\,\mu m^{-2}$. For temperature-dependent measurements, the sample was mounted in a cold finger cryostat. The use of a triple monochromator or appropriate notch filters allows recording of the Stokes as well as the anti-Stokes side of the PL.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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