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Thermal properties of CsPbCl$_3$ thin films across phase transitions

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Abstract

The local thermal conductivity, thermal diffusivity, and volumetric heat capacity of cesium lead chloride perovskite thin films are mapped simultaneously and with highest spatial resolution by a scanning near-field thermal microscope. Both, the 3D phase (CsPbCl$_3$) and the 0D phase (Cs$_4$PbCl$_6$) are investigated. For CsPbCl$_3$ thin films the variation of the thermal properties across the phase transitions in the range from room-temperature to 65 $^\circ$C are analyzed. While the thermal conductivity at room temperature is ultra-low, a significant increase of the thermal conductivity is found for the cubic phase of CsPbCl$_3$ ($T >$ 46 $^\circ$C). While only slight variations in the thermal conductivity are detectable for transitions from the monoclinic to the orthorhombic to the tetragonal phase, thermal diffusivity and volumetric heat capacity measurements are extremely sensitive to the amount of heat involved in the respective transition. It is shown that upon transition to the cubic phase of CsPbCl$_3$ thin films, the relative increase of the volumetric heat capacity is significantly higher than that of the thermal conductivity. Thus, the thermal diffusivity in the cubic phase becomes notably lower in comparison to that of the respective phase at room temperature. An increase of the volumetric heat capacity had been theoretically predicted earlier but could not be confirmed in previous experimental studies. The findings of our thermal analysis are of great general importance for fundamental material research and for the thermal design of thin-film devices based on CsPbCl$_3$ perovskites.

1. Introduction

Perovskite semiconductors are of tremendous interest for a variety of applications due to their relatively simple processing technology and their outstanding optoelectronic properties. Among them, all-inorganic perovskites are of particular interest for light emitting devices [1] and lasers [2] as organic–inorganic halide perovskites lack intrinsic stability [3, 4]. The phase transitions of all-inorganic lead halide perovskites, such as CsPbX$_3$ ($X = $ Cl, Br, I), are already known for a long time [5]. First detailed thermo-mechanical experimental investigations on both, CsPbCl$_3$ and CsPbBr$_3$ perovskites, have been made in order to understand the nature of the structural phase transitions already in the 1970s [6–8]. First and second order transitions from a monoclinic over an orthorhombic to a tetragonal structure at 310 K and 315 K, respectively, and a first order transition to a cubic structure at 320 K have been reported for CsPbCl$_3$ single crystals [6, 7]. These changes in the crystal structure have several consequences for the electronic properties of the material including changes in the dielectric constants and the band structures, which consequently alters the band gaps, their optical absorption properties, the carrier dynamics (charge carrier mobilities), etc. Furthermore, a structural phase transition may also lead to changes in the thermal expansion and the phonon structure that in turn affects the thermal conductivity, the thermal diffusivity, and the volumetric heat capacity. These intrinsic thermal properties should be investigated, as heat transport governs the ability to transport dissipated joule heat out of an operating device. Excessive parasitic heating may lead to thermally induced loss mechanisms and may ultimately infer thermally activated

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The thermal properties of CsPbX₃ perovskites at phase transitions have rarely been studied. For single crystals and powders a pulse transient method has been used [19, 20]. This method provides access to the specific heat c and thermal diffusivity a, while the thermal conductivity λ is determined indirectly via the relation

\[ \lambda = a \cdot \rho \cdot c \]

where \( \rho \) is the density and \( \rho \cdot c = c_{\text{vol}} \) is the volumetric heat capacity. These techniques did not evidence the expected behavior of \( c(T) \) when going from the monoclinic to the orthorhombic to the tetragonal phase of CsPbCl₃ [19]. Specifically, at a first order transition one would expect a divergence of \( c(T) \) due to the latent heat involved. Note, in case of CsPbCl₃ the measurement may be complicated as all these transitions occur within a temperature range of \( \Delta T \approx 10 \text{ K} \). On the contrary, for CsPbBr₃ the two phase transitions (orthorhombic-tetragonal-cubic) are separated by a \( \Delta T = 50 \text{ K} \) [20]. However, even though clear changes of \( c(T) \) could be observed, the behavior of \( c(T) \) did not agree with theoretical predictions.

Aside from these pulse transient methods, a variety of stationary and dynamic thermal measurement methods have been developed, which enable the simultaneous detection of thermal conductivity and thermal diffusivity [21–24]. These macroscopic methods are not suitable to measure thermal properties in thin films, as it is well known that thermal transport strongly depends on the dimensionality of the materials, e.g. with shrinking the thickness of thin films [25–27] where ballistic heat transport and phonon scattering at the interfaces significantly influence the diffusive heat flow [28–30].

On the other hand, we have recently shown that scanning near-field thermal microscopy (SThM) [31], which is a technique based on atomic force microscopy (AFM), is particularly suited to assess simultaneously thermal properties of lead-halide perovskite thin films. The interaction volume to determine thermal properties is ultra-small due to the width of the heater/thermometer probe \( w = 2 \cdot r_{\text{contact}} \) being on the order of 100 nm [32]. Using this technique we were able to determine the ultra-low thermal conductivity, thermal diffusivity, and small heat capacity of (3D) CsPbBr₃ and (2D) CsPb₂Br₅ thin films, at room temperature. By operating the SThM at two different frequencies simultaneously, we were able to record the thermal properties locally with highest spatial resolution.

In this work, we map the local thermal properties for 3D phase (CsPbCl₃) and the 0D phase (Cs₄PbCl₈) with highest spatial resolution for the first time. The thermal conductivity, thermal diffusivity, and volumetric heat capacity are analyzed simultaneously at the phase transitions in CsPbCl₃ perovskite thin films by using this advanced \( 3\omega \)-technique in SThM. A significant increase of both the thermal conductivity and the volumetric heat capacity at the transition to the cubic phase is demonstrated. Thus, theoretically predicted thermal properties could be confirmed experimentally for the first time.

2. Experimental

2.1. CsPbCl₃ thin film preparation

The low concomitant solubility of the starting materials CsCl and PbCl₂, even in highly polar solvents, prevented the deposition of a well-defined homogeneous and continuous CsPbCl₃ thin film from solution [33]. Thus, we used thermal evaporation. Individual layers of 10 nm CsCl and 5 nm PbCl₂ were deposited alternately to
produce a 200 nm thick pristine layer on glass substrates. Subsequently, a planar hot pressing process (PHP) was carried out with a pressing time of 30 min at 100 °C and a pressure of 100 bar to re-crystallize the film and to form the perovskite as reported earlier [2, 32]. This re-crystallization step affords thin films consisting of large crystals with a low surface roughness (∼1 nm rms) [34, 35]. The PHP process was performed in a home-built parallel-plate based imprint system. More details of the PHP process have been reported by us earlier [17]. All samples were kept under inert/vacuum conditions before and during measurement.

2.2. Measurement methodology

All perovskite thin films were initially characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence (PL). XRD was measured using a Panalytical Empyrean system with a Cu Kα anode (λ = 1.54056 Å). Note, for XRD, layers on glass substrates were used. SEM studies were carried out using a Philips XL30S FEG microscope with a field emission cathode. For PL measurements, a Nd:YVO laser (3rd harmonic, wavelength: 355 nm) was used. The PL spectra were dispersed in a monochromator (Princeton Instruments, Acton SP2500, gratings: 300 and 1200 lines mm⁻¹) and detected by a thermoelectrically cooled charge coupled device camera (Princeton Instruments).

The thermal measurement methodology is described in detail in [32]. Briefly summarized, the resistive thermal probe of the SThM (VITA-SThM probe from Bruker) is powered by a mixed signal of an adder at two AC currents $I_1^2 \sin(\omega_1 t)$ and $I_2^2 \sin(\omega_2 t)$ with angular frequencies $\omega_1$ and $\omega_2$. Thus, the resulting amplitudes of the local temperature variations $\hat{T}_{\text{probe}}(\vec{r})$:

$$\hat{T}_{\text{probe}}(\vec{r}) = \frac{\bar{Q}_I(\vec{r})}{\lambda(\vec{r})} = \left(\frac{1}{2}\right)^{\frac{1}{2}} \ln\left(\frac{a t^2}{150 \text{ nm}^2}\right) - \frac{1}{2} \ln(\omega) + \ln(2) - 0.5772$$

(1)

can be measured simultaneously at these frequencies, where $\bar{Q}_I(\vec{r})$ is the local heat flux into the sample. Since the self-heating resistive thermal probe of the SThM is always electrically powered by $P_{\text{el}} = 128 \mu W \pm 3 \mu W$, the local heat flux into the perovskite sample is given by $\bar{Q}_I(\vec{r}) = \frac{13.5 \mu W}{100 \text{ nm} \times \lambda_{\text{ave}}} \cdot P_{\text{el}} \cdot (\lambda(\vec{r})^2)$ [29, 36]. The differences of $\hat{T}_{\text{probe}}(\vec{r})_{32}$ and $\hat{T}_{\text{probe}}(\vec{r})_{33}$, obtained from the third harmonic signals, are used for direct quantitative thermal conductivity measurements [36–38]. In addition, the local thermal diffusivity $\hat{D}(\vec{r})$ is determinable indirectly from $\hat{T}_{\text{probe}}(\vec{r})_{\omega_{\text{min}}}$ using equation (1). The local volumetric heat capacity $\rho C(\vec{r})$ is finally given by the quotient of the thermal conductivity over the thermal diffusivity. Temperature dependent characterizations of these thermal properties at phase transitions above room temperature are carried out heating the sample resistively. The sample temperature is measured with a PT100 element controlled by measuring $\frac{dR}{dT}$ of the probe on top of the sample surface. A heat sink is mounted to protect the z-piezo of the AFM, allowing measurement up to 150 °C.

3. Results

3.1. Mapping thermal properties of Cs₃Pb₅Cl₇ perovskite thin films

In this work, we analyze the topography, the local thermal conductivity, the local thermal diffusivity, and the local volumetric heat capacity of Cs₃Pb₅Cl₇ perovskite thin films with high spatial resolution by using the SThM operated at two different frequencies simultaneously [32]. The Cs₃Pb₅Cl₇ thin films studied in this work were obtained by re-crystallization of thermally evaporated PbCl₂/Cl₅ multi-layers using a thermal imprint process (see experimental and figure 1(a)). The resulting layers are smooth with a rms roughness of 1.8 nm. An initial study by backscattered scanning electron microscopy (SEM) revealed a notable contrast (figure 1(b)). Note, a similar contrast has previously been evidenced by electron backscatter diffraction (EBSD) for Cs₅Pb₁₀Br₁₂ perovskite thin films that had undergone a similar procedure [2, 32], where the contrast could be clearly assigned to CsPbBr₃ (3D) and CsPb₂Br₅ (2D) grains in the film. In the present case, the coexistence of 3D phase CsPbCl₃ and the 0D phase Cs₃Pb₅Cl₇ has been confirmed by XRD (figure 1(c)). Note, the diffraction peaks were assigned by comparing with corresponding single crystal and powder diffractograms [39–41]. The dominance of the 100, 200 and 111, 222 peaks for CsPbCl₃ and Cs₃Pb₅Cl₇, respectively, indicates the high degree of orientation of the crystals as a result of the re-crystallization in the PHP process. In a correlation of XRD and SEM data, we assign the 3D phase (CsPbCl₃) in the thin film to the substantially brighter regions in the SEM image compared to the darker areas corresponding to the 0D phase (Cs₃Pb₅Cl₇). Similar to our earlier findings on cesium led bromide, the contrast is a result of the substantially different relative concentration of Pb in the 0D and 3D grains (see figure 1(b)). Due to primary electron channeling effects a slight contrast variation of the bright CsPbCl₃ grains can be explained. The high quality of the 3D-CsPbCl₃ thin film is verified by the PL spectra with a maximum at 413.4 nm and a FWHM of 10 nm (figure 1(d)), which fits nicely to this of single crystals [39].
the grain boundaries as well as in smaller grains of Cs4PbCl6 perovskites, which might be explained by a higher vibrational energy in these grains.

band structure calculations on 0D perovskites [41].

Our SThM technique simultaneously provides topography data (figure 1(e)) and the local thermal conductivity $\lambda(\vec{r})$ (figure 1(f)) with a high spatial resolution of less than 100 nm. Significant local variations of the thermal conductivity within the measured area of 10 $\mu$m $\times$ 10 $\mu$m are obtained.

Correlating our SThM data with the insights gained from XRD/SEM, one can attribute the thermal conductivities of 0.49 $\pm$ 0.04 and 0.30 $\pm$ 0.03 W/(m K) to the 3D phase (CsPbCl3) and the 0D phase (Cs4PbCl6), respectively (see figure 1(e)). Since the thermal conductivity of CsPbCl3 is found to be very similar to that of MAPbCl3 (0.50 $\pm$ 0.05 W/(m K)) at room temperature [17], it indicates that the thermal conductivity is mainly dominated by the Pb-Cl cage scaffold and the lead-halide bond [14, 15]. On the other hand, the significantly lower thermal conductivity found for Cs4PbCl6 agrees well with the findings obtained from phonon band structure calculations on 0D perovskites [42], which reveal low group velocities and localization of vibrational energy in these grains.

Aside from the thermal conductivity, an average thermal diffusivity of $0.5 \pm 0.1$ mm$^2$ s$^{-1}$ was determined for the CsPbCl3 film in (a). Only slight differences $\Delta a(\vec{r})$ are detected for CsPbCl3 and Cs4PbCl6 within this film in (a). The image (b) shows the local variations of the volumetric heat capacity $c_{vol}(\vec{r})$ of the CsPbCl3 film. The deviation of the volumetric heat capacity $\Delta c_{vol}(\vec{r}) = \Delta \lambda(\vec{r})/\Delta a(\vec{r})$ in (c) varies significantly within Cs4PbCl6 grains and at their boundaries.

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Aside from the thermal conductivity, an average thermal diffusivity of $0.5 \pm 0.1$ mm$^2$ s$^{-1}$ was determined for the cesium lead chloride layers using the measured $T_{\text{probe}}(\vec{r})$ ($\Delta t$) (see figure S1 in supporting information available online at stacks.iop.org/JPMATER/3/024004/mmedia) and the determined thermal conductivity $\lambda(\vec{r})$ (equation 1)) for the whole film. This value for $\alpha(\vec{r})$ is in good agreement to the results obtained for CsPbCl3 single crystals using transient methods [20]. Because $\alpha(\vec{r})$ depends exponentially on $T_{\text{probe}}(\vec{r})$ as well as on $1/\lambda(\vec{r})$ the uncertainty in the absolute value is relatively high. Nevertheless, only minor local variations of $\alpha(\vec{r})$ (i.e. $\Delta a(\vec{r})$) of about $0.05 \pm 0.01$ mm$^2$ s$^{-1}$ occur, as illustrated in figure 2(a). Note, the thermal diffusivity for CsPbCl3 and large Cs4PbCl6 crystallites is found to be very similar. Moreover, only a small contrast appears at the grain boundaries as well as in smaller grains of Cs4PbCl6 perovskites, which might be explained by a higher density of structural defects. This small contrast might be the reason, why lead halide perovskite thin films make
Table 1. Summarized thermal properties of cesium lead chloride perovskite thin films at RT.

| Phase       | Thermal conductivity (W/(m K)) | Thermal diffusivity (mm² s⁻¹) | Volumetric heat capacity (J/(cm³ K)⁻¹) | Specific heat capacity (J/(g K)) |
|-------------|--------------------------------|------------------------------|----------------------------------------|---------------------------------|
| 3D phase CsPbCl₃ | 0.49 ± 0.04                    | 0.5 ± 0.1                    | 0.9 ± 0.1                               | 0.22 ± 0.07                     |
| 0D phase Cs₂PbCl₆ | 0.30 ± 0.03                    | 0.5 ± 0.1                    | 0.5 ± 0.2                               | 0.15 ± 0.08                     |

thermal diffusivity measurements challenging. In this context, it must be noted that, experimental studies of thermal properties on 0D Cs₂PbCl₆ perovskites are not reported at all, as of yet.

Since \( a(\vec{r}) = \frac{\lambda(\vec{r})}{\rho(\vec{r}) c(\vec{r})} \), the volumetric heat capacity \( c_{\text{vol}}(\vec{r}) = \rho(\vec{r}) c(\vec{r}) \) is of interest, as it ultimately tells the ability to store the supplied heat. Variations of \( c_{\text{vol}}(\vec{r}) \) can even lead to discontinuous temperature gradients in dynamically operated electrical systems [43]. Assuming isotropic heat transport as the most simple approximation, an average volumetric heat capacity of 0.9 ± 0.1 J/(cm³ K) and 0.5 ± 0.2 J/(cm³ K) results for the 3D and 0D regions of the perovskite film, respectively (see figure 2(b)). Please note that in general thermal conductivity and diffusivity are tensors. However, in the most simple approximation we consider 3D (CsPbCl₃) and 0D (Cs₂PbCl₆) as isotropic materials. The corresponding specific heat capacities \( c_{\text{CsPbCl}_3} = 0.22 \pm 0.07 \) J/(g K) and \( c_{\text{CsPbCl}_6} = 0.15 \pm 0.08 \) J/(g K) were determined by taking the mass densities of \( \rho_{\text{CsPbCl}_3} = 4.24 \) g cm⁻³ [44] and \( \rho_{\text{CsPbCl}_6} = 3.28 \) g cm⁻³ [45] into account (summarized in table 1). Note, earlier studies using a pulse transiente technique found significantly higher values of \( c_{\text{CsPbCl}_3} = 0.27 \) J/(g K) to 0.35 J/(g K) [19, 20]. The specific heat capacity of CsPbCl₃ in the monoclinic phase is smaller than that of CsPbBr₃ thin films at the orthorhombic structure \( (c_{\text{CsPbBr}_3} = 0.29 \pm 0.09 \) J/(g K)) at RT [32].

It is important to note, that both the density and the heat capacity may significantly differ due to local internal stress, etc. Hence, the local deviation of the volumetric heat capacity \( \Delta c_{\text{vol}}(\vec{r}) = \Delta c(\vec{r}) = \Delta \lambda(\vec{r}) / \Delta a(\vec{r}) \) is evaluated to clarify inhomogeneities within the grains. As can be seen from figure 2(c), \( \Delta c_{\text{vol}}(\vec{r}) \) is four orders of magnitude less than \( c_{\text{vol}}(\vec{r}) \) in the films, indicating that effects like stress etc are negligible. However, the highest deviations are found at the grain boundaries as well as for small grains of 0D, while the contrast and thus \( \Delta c_{\text{vol}}(\vec{r}) \) is low in the larger 0D regions. A possible explanation for the local deviation of the volumetric heat capacity near the grain boundaries may be lattice defects.

Taken together, the measurement methodology allows us to detect simultaneously the local thermal conductivity, the local thermal diffusivity, and the local volumetric heat capacity separately for 3D phase CsPbCl₃ and the 0D phase Cs₂PbCl₆. Note, our technique is not influenced by the sample temperature.

3.2. Thermal properties of CsPbCl₃ perovskite thin films at phase transitions

In particular, in the case of CsPbCl₃ elevated moderate temperatures can give rise to phase transitions from a monoclinic to orthorhombic to tetragonal to cubic phase. Here, we analyze the thermal properties, \( \lambda(\vec{r}) \), \( a(\vec{r}) \), and \( c_{\text{vol}}(\vec{r}) \), of CsPbCl₃ perovskite thin films as a function of temperature, upon increasing the temperature of the perovskite samples starting at RT.

As can be seen from our direct measurements shown in figure 3, only minor changes of the average thermal conductivity in CsPbCl₃ perovskite thin films appear for temperatures between room temperature (RT) and 36 °C, where the crystal is in its monoclinic phase. A very slight decrease of \( \lambda \) occurs between 37 °C and 41 °C (orthorhombic phase). In the tetragonal phase, between 42 °C and 46 °C, the thermal conductivity of the CsPbCl₃ thin film shows a slight increase back to values found in the monoclinic phase below 36 °C. While these variations are only marginal, a significant increase of \( \lambda_{\text{CsPbCl}_3}(T) \) by a factor of three to a level of 1.60 ± 0.08 W/(m K) is clearly detected at \( T > 46 °C \), where the material assumes its cubic phase. This behavior has been predicted theoretically, due to a significantly higher group velocity of acoustic phonons in the cubic structure compared to that in the tetragonal or orthorhombic phase [14]. We have found a similar behavior at the tetragonal to cubic transition in MAPbI₃ single crystals. [14]

In a next step, the average thermal diffusivity and the average volumetric heat capacity of the CsPbCl₃ perovskites thin films were determined across its phase transitions, as illustrated in figure 4. Importantly, the thermal diffusivity varies notably for the different crystal phases. As discussed above, the deviations of the average \( a(T) \) and \( c_{\text{vol}}(T) \) can be measured with better accuracy than the respective absolute values. Thus, in contrast to earlier transient measurements on a single crystal [19, 20], our technique allows us to unambiguously separate the thermal properties of the different phases. Surprisingly, in the orthorhombic structure, the highest thermal diffusivity of 0.7 ± 0.1 mm² s⁻¹ occurs, even though the thermal conductivity is minimum there (see figure 4(a)) and a considerable acoustic attenuation was observed by neutron scattering experiments in this temperature range [46]. The experimentally determined increase of \( a(T) \) results in a concomitant decrease of \( c_{\text{vol}}(T) \) as \( c_{\text{vol}}(T) \) is derived by \( \lambda(T)/a(T) \) (see figure 4(b) (please note the log scale on the ordinate)).
smooth variations at the relating first and second order transitions at low temperatures, an abrupt increase of the average volumetric heat capacity is obtained on the CsPbCl₃ perovskites thin film at the first order transition to the cubic phase at 47 °C. Finally, $c_{\text{vol}}(T) = 4.1 \pm 0.4$ J/(cm³ K), is more than 4 times higher in the cubic structure compared to the other phases. This increase can be understood due to the highest degree of freedom for the rotational modes of PbCl₆ octahedra around the three principal axes in the cubic phase [46]. Thus, considering the variation in $\lambda(T)$ and $c_{\text{vol}}(T)$, the thermal diffusivity $a(T)$ in the cubic phase, after going through a minimum of $0.2 \pm 0.1$ mm² s⁻¹ at around 51 °C, saturates at $0.4 \pm 0.1$ mm² s⁻¹ and is smaller than that of the other phases at lower temperature.

Finally, it must be mentioned, in contrast to our investigations and theoretical predictions, the former transient measurements on single crystals showed a lowered specific heat capacity in the cubic structure compared to the monoclinic phase. An abnormal characteristic of the thermal diffusivity was also observed and the thermal diffusivity at room temperature is less than that at higher temperatures in the cubic phase.

4. Conclusion

For the first time a comparative experimental assessment of thermal conductivity, thermal diffusivity, and volumetric heat capacity of CsPbCl₃ thin films across phase transitions has been performed by the application of a measurement technique in the frequency domain based on scanning near-field thermal microscopy. An ultralow average thermal conductivity of $0.49 \pm 0.05$ W/(m K), low thermal diffusivity of $0.5 \pm 0.1$ mm² s⁻¹, and small volumetric heat capacity of $0.9 \pm 0.1$ J/(cm³ K) have been found for CsPbCl₃ films. Besides, an ultralow thermal conductivity of $0.30 \pm 0.03$ W/(m K) and small volumetric heat capacity of
0.5 ± 0.2 l/(cm² K) have been determined for the 0D phase Cs₄PbCl₆. Accordingly, the average thermal diffusivity \( a(T) \) is quite similar for these 3D CsPbCl₃ and 0D CsPbCl₆ films at room temperature. Direct mapping of the local thermal conductivity of 3D CsPbCl₃ thin films in dependence on the sample temperature, a significant increase of the average thermal conductivity up to 1.60 ± 0.05 W/(m K) for the cubic phase at \( T > 46 \) °C is obtained. Although very slight variations of \( \lambda(T) \) appear at the phase transitions monoclinic-orthorhombic-tetragonal, the variations of the thermal diffusivity correlate significantly with these first and second order transitions. It is shown that in the cubic phase the volumetric heat capacity showed significantly higher relative increase compared to that of the thermal conductivity.

In particular, our measurements have shown that capturing the characteristics of the volumetric heat capacities in dependence on the temperature is a challenge and requires particular attention. Upon transition to the cubic phase, a first order phase transition could be confirmed for CsPbCl₃. We believe that our insights will be of great general importance for the fundamental material research as well as for the thermal design of thin-film devices based on halide perovskites.

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