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One- and two-photon spectroscopy of Ce^{3+} ions in $\text{LaF}_3\text{--CeF}_3$ mixed crystals*

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Abstract. Absorption, excitation and emission spectra and lifetime measurements in cerium-doped lanthanum fluoride single crystals were obtained using both one- and two-photon spectroscopy techniques. It is shown that two kinds of fluorescent centres are present. In weakly doped systems, a rapid fluorescence around 300 nm dominates, due to Ce^{3+} ions at normal sites. In heavily doped systems, an additional longer fluorescence appears at higher wavelengths due to Ce^{3+} ions occupying perturbed sites and acting as traps. In CeF_3 , the energy migrates among Ce^{3+} ions and is finally trapped so that only the trap emission is detected at room temperature. Significant energy losses in the fluorescence of Ce^{3+} at normal sites are explained by up-conversion and ionization processes and by non-radiative surface recombination phenomena for the case of strong absorption. Two-photon excitation spectra in the region of trap absorption confirm the role of traps in emission mechanisms and show narrow lines which could be vibronic structures of various kinds of traps existing in these materials.

1. Introduction

There is at present great interest in the use of scintillating materials as components of high-performance electromagnetic calorimeters to be used in the new generation of accelerators. Their designed luminosities are very high and introduce new constraints on the crystals: they must have a fast response, be radiation hard and as dense as possible for calorimeter compactness. Several crystals and glasses should have the desired properties. Cerium fluoride CeF_3 and cerium-doped lanthanum fluoride Ce:LaF_3 are two of them, since their scintillation properties were recently discovered [2–5]. The search for tunable solid-state laser materials is another very important field of research for application; it was suggested [6] and later demonstrated [7] that ultraviolet lasing was possible in Ce^{3+} -doped LaF_3 with high power output and tunability in the 306–330 nm region.

Due to the interest in such $\text{LaF}_3\text{--CeF}_3$ mixed crystals for applications, it is very important to understand the fluorescence mechanisms occurring in these systems. The few papers which report on the spectroscopy of cerium in lanthanum fluorides do not provide an explanation of the fluorescence process in the case of heavily

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doped compounds [5, 8]; the main purpose of this article is therefore to interpret the change in the absorption and fluorescence spectra and in the fluorescence lifetimes when the cerium concentration and the temperature are varied. In particular, it is shown that processes such as fast energy migration, up-conversion and non-radiative surface recombination do arise in heavily doped systems and that these processes can strongly modify the fluorescence properties.

2. Experimental details

The $\text{La}_{1-x}\text{Ce}_x\text{F}_3$ crystals were grown by R Sparrow (from the Optovac company) using the Bridgman technique. Samples containing various amounts of cerium were studied: $x = 0.0005$; 0.01; 0.05; 0.10; 0.50; and 1.0.

The absorption spectra were obtained in the 200-300 nm range on a CARY 2300 spectrophotometer equipped with an SMC liquid-helium cryostat for low-temperature measurements.

The fluorescence was excited at 228 nm with a Q-switched Nd^{3+} :YAG pumped-dye laser (YAG 481 + TDL IV model from Quantel) and frequency doubling and mixing systems. The fluorescence was analysed with a Hilger computer-scannable 1 m monochromator and detected with a Hamamatsu R1477 photomultiplier tube (PMT). The amplified signal was then fed into the ADC board of a microcomputer. Fluorescence lifetimes were recorded under laser excitation (pulse width ≈ 10 ns) using a Stanford SR430 multichannel analyser with a resolution of 5 ns per channel. The excitation was obtained utilizing UV synchrotron radiation from the SUPERACO positron storage-ring facility (LURE) of Orsay university, and a 3 m home-made vacuum UV monochromator.

The experimental set-up used for the two-photon absorption study comprised an XeCl 308 nm excimer pump laser (Excimer-500 model from Lumonics) and a dye laser (Hyperdye-300, Lumonics). Various coumarin dyes were used to cover the range of interest from violet to green. The laser beam was focused on the sample (which was placed in a cryostat) and the UV fluorescence was observed at right-angles through an 8 nm band-pass monochromator (H20, Jobin-Yvon). In order to suppress completely the laser light passing through the monochromator, we placed a 10 nm bandwidth UV filter (centred at 325 nm) in front of the entrance slit of the monochromator. The fluorescence was detected by a photomultiplier tube (EMI 6256 S) and the output signal was sent through a delay line to an averager-integrator boxcar (PAR 165 and 162) and finally converted into a digital signal by an AD converter coupled to a computer. The intensity of the incident laser beam (reference signal) was measured with a joulemeter (Molelectron) for calibration.

3. Results and discussion

3.1. One-photon spectroscopy

The absorption spectrum of a very weakly Ce^{3+} -doped LaF_3 sample is shown in figure 1. Four peaks were detected in the 200-250 nm range, in agreement with previous observations [8]. Also, a fifth one was observed in the UV vacuum region [9] and it will be seen later that fluorescence excitation spectra confirm the existence of five absorption peaks. This reflects the $4f \rightarrow 5d$ transitions where the 5d state is

split into five levels, as expected from the low cation site symmetry found in LaF₃. It is well established now that the tysonite structure of LaF₃ and CeF₃ has the space group D_{3d}⁴, wherein the cation occupies a site with local symmetry C₂ [10, 11]. The absorption bands can be deconvoluted into Gaussians and the oscillator strength, f , of the absorption transition from the ground state to the lower 5d level was deduced experimentally using the well known equation [12]:

$$\int \sigma(\nu) d\nu = (\pi e^2 / mc) [(E_{\text{eff}} / E_c)^2 (1/n)] f \quad (1)$$

which is valid in the electric-dipole case. $\sigma(\nu) = k_\nu / N_V$ is the absorption cross section, where k_ν is the absorption coefficient at frequency ν (cm⁻¹) and N_V is the density of absorbing centres (cm⁻³), and n is the index of refraction ($n \simeq 1.65$ [5])—the Lorentz local-field expression

$$E_{\text{eff}} / E_c = (n^2 + 2) / 3 \quad (2)$$

may be used for rare-earth impurities in crystals [13]. The integral $\int k_\nu d\nu$ represents the area of the absorption band in cm⁻². Knowing the cell dimensions and that the unit cell of the LaF₃ crystal contains six molecules [10], we calculated that a concentration of 0.05 at.% corresponds to $N_V = 9.1 \times 10^{18}$ cm⁻³. Finally, the oscillator strength f was found to be equal to 2.74×10^{-3} ; this is very close to the calculated value (3.20×10^{-3}) deduced by Starostin *et al* from a crystal-field calculation [14].

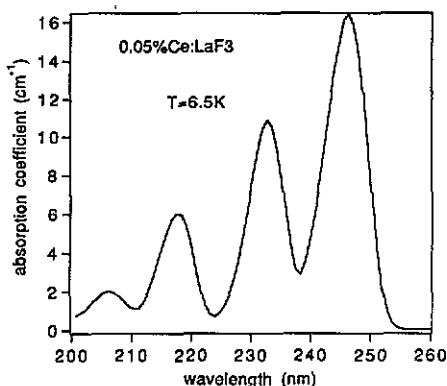


Figure 1. Absorption spectrum of Ce:LaF₃ at low temperature.

The emission spectra are pictured in figure 2 for various Ce³⁺ contents. At low concentrations, the spectra have two peaks resulting from transitions from the lowest 5d level to the two spin-orbit split ground states, ²F_{5/2} and ²F_{7/2}. An additional broad band grows on the low energy side as the Ce concentration increases. This band is due to the emission from traps which is enhanced tremendously by a fast energy migration among the Ce³⁺ ions in samples of high Ce concentration. These traps are probably cerium ions in varyingly strongly perturbed sites, giving rise to an inhomogeneously broadened emission band. Actually, the most effective perturbations could occur in the environment of Ce³⁺ nearest to fluorine ions (for example an F⁻ vacancy or an F⁻ ion in an interstitial position). The rare-earth atoms have an

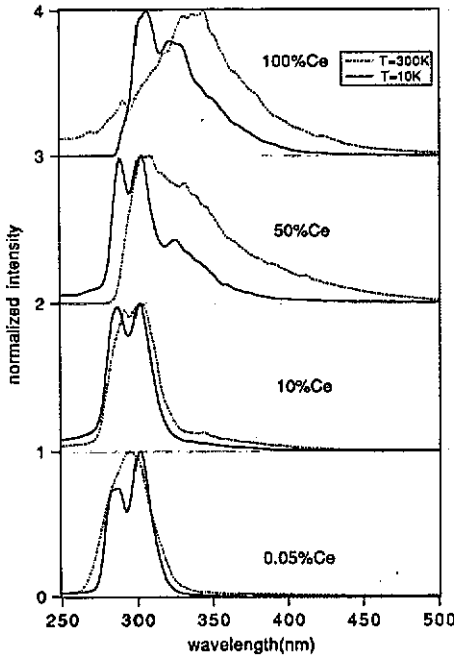


Figure 2. Emission spectra of variously Ce-doped LaF_3 at low and room temperatures.

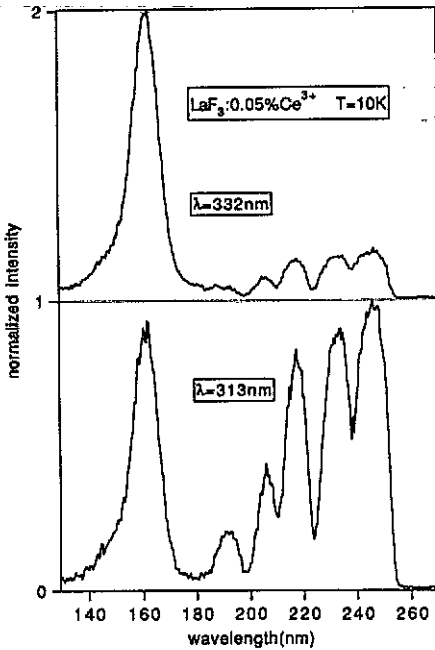


Figure 3. Fluorescence excitation spectra of a weakly Ce-doped LaF_3 crystal at low temperature for two emission wavelengths.

elevenfold coordination of F atoms with distances between 2.421 and 2.999 Å (LaF_3) and 2.400 and 2.974 Å (CeF_3) [11]. Such coordination around Ce can explain the large inhomogeneous broadening. It should be noted that the normal Ce emission bands

are also inhomogeneously broadened due to small changes of the local crystal field experienced by Ce fluorescent centres. The relative intensity of the trap emission increases with temperature, indicating that the $Ce^{3+} \rightarrow Ce^{3+}$ energy diffusion is enhanced by thermal assistance. It is clear that in CeF_3 at room temperature, the trap emission strongly dominates.

Fluorescence excitation spectra of the weakly doped sample (0.05% Ce) in figure 3 show five peaks in the near-UV range above 180 nm which describe the $4f \rightarrow 5d$ transitions, as expected from the low cation site symmetry. The four peaks observed above 200 nm in both the absorption and the excitation spectra have their maxima at the same energies. The UV vacuum band observed near 161 nm can be assigned to $4f \rightarrow 6s$ transition or some charge transfer processes such as $F^-(2p^6) \rightarrow Ce^{3+}(6s)$ [8, 15], both involving the $6s$ level. High-energy excitation in this level probably gives rise to photoionization of Ce^{3+} ions, leading to the creation of Ce^{4+} ions which are stable in many compounds. This phenomenon could explain why the relative strength of the transitions to $5d$ and $6s$ levels is so strongly dependent on the region of the fluorescence spectrum considered here (figure 3). In particular, the system excited in the $6s$ level exhibits a relatively much more intense trap fluorescence (332 nm) than normal Ce^{3+} fluorescence (313 nm). Let us suppose that the main kind of trap in the weakly doped sample is a Ce^{3+} ion close to a Ce^{4+} ion. The free electron resulting from the photoionization of Ce^{3+} would immediately be trapped by the nearby Ce^{4+} ion so that the $Ce^{3+}-Ce^{4+}$ pair is unchanged, as is the trap fluorescence. On the other hand, the $6s$ excitation of Ce^{3+} ions lying at normal sites would lead to a strong decrease of their fluorescence due to energy losses by photoionization.

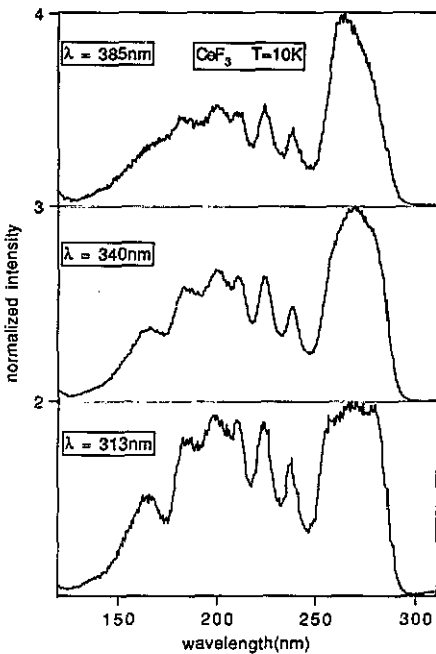


Figure 4. Fluorescence excitation spectra of CeF_3 at low temperature for various regions of the emission spectrum.

Let us consider now the excitation spectra of heavily doped samples. Figure 4 represents the spectra of CeF_3 for various fluorescence domains. It is clear that

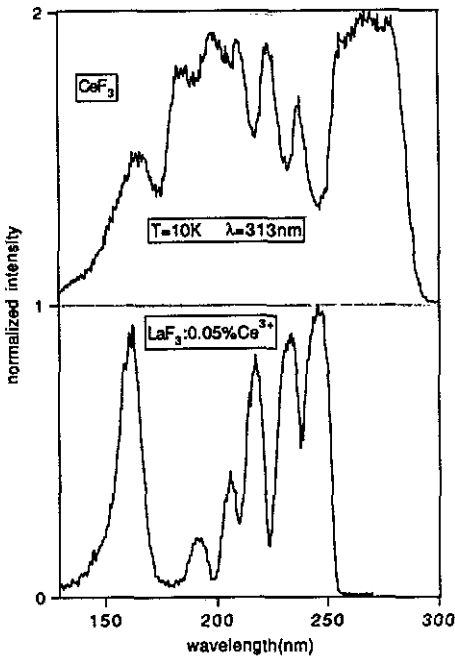


Figure 5. Comparison of fluorescence excitation spectra of 0.05% Ce:LaF₃ and CeF₃ at low temperature.

new structures appear above 250 nm and their relative intensities increase as the fluorescence considered is shifted to the red, which is where the trap emission mostly arises. These new low-energy fluorescence excitation bands are therefore assigned to traps. Below 250 nm, five peaks are detected in the energy range of the $f \rightarrow d$ transitions, but they are strongly blue-shifted compared to the peaks observed in the weakly doped compound (figure 5). However, the absorption spectrum of a thin film of CeF₃ [9] shows that the five peaks arise at the same energy as those observed in weakly doped samples. In fact the maxima of absorption are exactly correlated to the minima of fluorescence excitation. It seems that in a previous paper (figure 2 of [16]) this phenomenon was observed in 5% Ce:LaF₃, but was not recognized. This phenomenon must therefore be related to energy-loss mechanisms which must be strongly Ce-concentration dependent, since holes are only detected in samples containing more than 1% Ce³⁺ ions. Up-conversion energy transfers, involving two ions in the excited state and which can be efficient in rare-earth doped systems when the concentrations are high enough, could be a source of energy loss. This phenomenon must involve the conduction band of the crystal to explain the drop of the fluorescence efficiency. Of course these mechanisms are not observed in the case of traps, because of the low trap concentration, and under two-photon excitation (see below), which provides too few Ce³⁺ ions in the excited state.

Lifetime measurements were recorded for different concentrations and at various fluorescence wavelengths. The decays are very short (a few tens of ns), as expected from the allowed electric-dipole transitions. Our set-up did not allow us to describe accurately the profiles of the decays, especially shortly after the laser pulse. The decays were found to be roughly exponential and weakly temperature dependent. The various measured time constants are gathered in table 1. The lifetime of the Ce³⁺

fluorescence (short-wavelength emission) tends to shorten when the Ce concentration increases as a result of the energy migration between Ce³⁺ ions. This trend cannot be checked further in samples of high Ce concentration because of the growing importance of the trap emission, even in the short-wavelength region. The time constant increases with the fluorescence wavelength. The radiative lifetime τ_0 of the emitting level for the electric-dipole case can be expressed as [12]

$$\tau_0 = 1.51(3/n^2 + 2)^2(\lambda_0^3/nf) \quad (3)$$

where λ_0 is the wavelength (in m) of the radiation in the vacuum, n is the index of refraction and f is the oscillator strength of the emission transition. In going from Ce³⁺ ions at normal sites to traps, τ_0 and λ_0 increase. The wavelength dependence of n is not known for LaF₃ and CeF₃, but, as in most materials, it is expected to decrease when the wavelength increases. A reasonable estimate of $\Delta n = n(300 \text{ nm}) - n(400 \text{ nm})$ of about 0.05 leads to an increase of τ_0 by a factor two. Similar experimental variation is observed in 10% Ce³⁺:LaF₃ (table 1), indicating that the oscillator strength of the emission transition is nearly the same for normal and perturbed Ce³⁺ centres. This could be explained by the very low site symmetry of Ce³⁺, which is not significantly lowered when the next neighbouring environment of the centre is modified. Similar variations of τ_0 are detected across the inhomogeneous broad emission band of traps in CeF₃ (table 1), which can be interpreted the same way.

Table 1. Fluorescence decay time constants (ns) of various Ce-doped LaF₃ samples for different fluorescence wavelengths.

Ce concentration	Temperature	Fluorescence wavelength (nm)					
		280	300	310	320	360	450
0.05%	10 K		21.0				
10%	10 K	18.4		17.0		32	
50%	10 K					29.5	
100%	10 K				26	29.5	48
	300 K				25	29.0	37

3.2. Two-photon spectroscopy

We saw previously that, for all the Ce:LaF₃ samples with the exception of the very weakly doped (0.05% Ce) system, the one-photon fluorescence excitation spectra exhibited dips well correlated to the maxima of the absorption spectra, and we ascribed this phenomenon to some kind of up-conversion processes leading to significant energy losses when the population of the lowest excited state of Ce is large enough.

One- and two-photon spectroscopy techniques are usually very complementary to each other. The transition selection rules are different: for example a parity-forbidden one-photon transition corresponds to a parity-allowed two-photon transition. Regarding this aspect, two-photon absorption seems not to be of interest at first sight in the present case since the interconfigurational $f \rightarrow d$ transitions are already parity-allowed in one-photon spectroscopy, but, in principle, parity-forbidden in two-photon spectroscopy. For the case of a non-centrosymmetrical site, however, the crystal field

Hamiltonian does not commute with the parity operator and has therefore even and odd terms, the latter mixing the states of opposite parities. Therefore, $f \rightarrow d$ transitions in Ce:LaF_3 are then partially parity-allowed in two-photon spectroscopy. In the present case, we take advantage of the two-photon excitation by the fact that only a few Ce^{3+} ions can be excited, allowing the avoidance or reduction of the energy losses by up-conversion mechanisms, as in the case for strongly dispersed media. Another advantage is that the investigation in the UV range can be done using visible photons.

The two-photon fluorescence excitation spectrum of 5% Ce:LaF_3 was recorded at very low temperature and is compared in figure 6 with one-photon spectra. It appears that the two excitation spectra are very different: the two-photon spectrum exhibits resolved peaks at the same energies as the one-photon excitation peaks of 0.05% Ce:LaF_3 , while the one-photon excitation spectrum of 5% Ce:LaF_3 shows non-resolved bands reflecting significant fluorescence intensity losses.

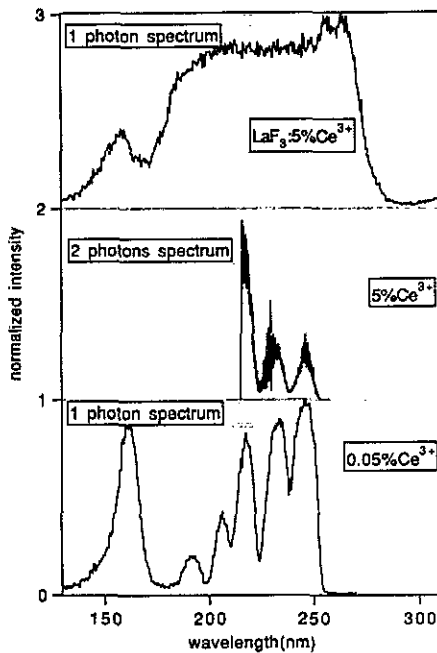


Figure 6. One- and two-photon excitation spectra of 5% Ce:LaF_3 at low temperature. Comparison with one-photon absorption spectrum of 0.05% Ce:LaF_3 .

Luminescent emission excited by two-photon absorption has the other advantage of originating in the bulk of the sample. This is particularly important with strongly absorbing systems, in which one-photon excited emission usually originates from the surface layers. It turns out that in addition to the up-conversion processes which probably occur in our systems, another probable source of losses could be non-radiative surface recombination, which becomes dominant as the absorption coefficient increases and the exciting light is absorbed closer to the sample surface.

We have recorded two-photon laser excitation spectra in the region of trap absorption on the lower energy side of the lowest d emitting level of Ce^{3+} . The spectrum of CeF_3 was obtained at 170 K (figure 7(a)) by selecting the fluorescence using a 250–400 nm bandpass filter. It shows in the $2 \times 250 \text{ nm} - 2 \times 265 \text{ nm}$ region a broad

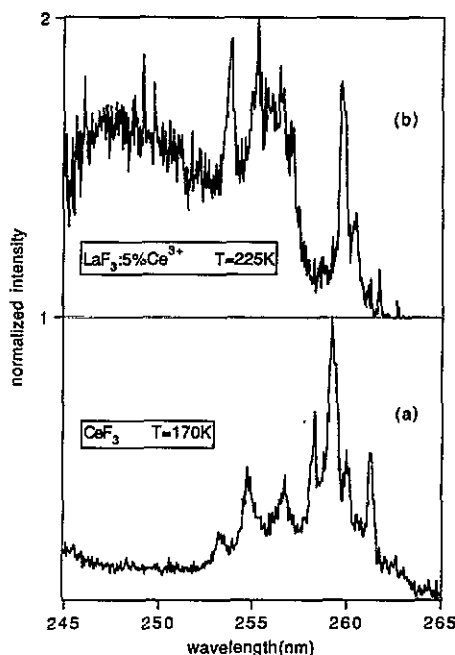


Figure 7. (a) Two-photon excitation spectrum of CeF₃ in the region of the lowest excited state. Filter bandpass: 250–400 nm. (b) Two-photon trap fluorescence excitation spectrum of 5% Ce:LaF₃ in the region of the lowest excited state.

band with a superposition of narrow lines which can be detected due to the good resolution of the laser excitation. As mentioned previously, the broad band (and many others arising in a wider wavelength range and which were not resolved in the one-photon excitation spectra) is probably due to Ce³⁺ ions occupying strongly perturbed sites. Narrow lines could be due to some other impurity rare-earth ions introduced with Ce³⁺ in the crystal. However, the UV fluorescence excitation spectra are not typical of any rare-earth ions. The narrow lines could be rather the vibronic structures of the various kinds of traps existing in the materials. If this is true, similar structures should be observed for Ce³⁺ ions in normal sites; we intend to determine their existence in further work at very low temperature. The lowest d excited state of Ce³⁺ at a normal site was not detected in CeF₃. On the other hand, in 5% Ce:LaF₃, the traps were detected beside the lowest energy band of Ce³⁺ (figure 7(b)).

4. Conclusion

One- and two-photon spectroscopy of Ce³⁺ ions in LaF₃–CeF₃ mixed crystals has led to a good understanding of the fluorescence processes arising in heavily doped crystals, including CeF₃, and which were never correctly interpreted in the past. It is clear that in such compounds the mechanisms are completely governed by traps because of the very fast energy migration among the Ce³⁺ ions. It has also pointed out an important drop in the fluorescence efficiency which can be interpreted by the occurrence of other processes like up-conversion and non-radiative surface recombination.

The exact nature of the traps is still an open question, as is often the case in many fluorescent doped materials. The main traps are probably perturbed Ce³⁺ centres,

since their spectroscopic characteristics are similar to unperturbed Ce^{3+} ions.

The purity of scintillating materials is a very important problem, since it is often directly related to the radiation damage. We intend to do our utmost to identify the nature of the traps by working with crystals of various origins, some grown with ultra-pure starting materials, and by using the two-photon spectroscopy techniques which have proved very helpful. Such work is now in progress.

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