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Full Length Article

About spectroscopy of $CeF_3:Nd^{3+}$ crystal and the first laser experiments with diode pumping

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ABSTRACT

The CeF_3 crystal samples activated by neodymium ions were grown by the Bridgman method and studied under diode pumping. Spectroscopic studies were carried out for calculations of the lasing threshold, because some data for these calculations were not available in the literature or are not quite correct. As a result, the spectroscopic data on the $CeF_3:Nd^{3+}$ crystal available in the literature have been supplemented and corrected. It has been determined that concentration quenching occurs at concentrations not higher than 1.5%. Based on the obtained data, the threshold of oscillations at the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of Nd^{3+} ions was estimated to be about 2.3 mJ. In the first experiments with diode pumping, lasing was obtained at a wavelength of 1064 nm on the $CeF_3:Nd^{3+}$ crystal with a slope efficiency of 25%. The obtained experimental results agree with the theoretical estimate of the lasing threshold.

1. Introduction

One of the main issues of modern laser physics is the creation of compact and powerful diode-pumped lasers. In this regard, crystals activated with rare earth elements with a high level of activation are of particular interest. Based on such crystals, it is possible to create microlasers with high-energy characteristics. For example, crystals $CeF_3:Nd^{3+}$ according to the literature [1] do not exhibit luminescence quenching up to an activation level of 4%. In this case, a specific energy output comparable to conventional lasers can be achieved.

The literature data on the possibility of a high level of doping of the $CeF_3:Nd^{3+}$ crystal without significant loss of luminescence intensity attracted our attention. More detailed data on the laser properties of the crystal were needed. At first glance, the optical properties of this crystal have been studied enough detail but there are no studies of its diode-pumped laser properties. Moreover, some of the spectroscopic data necessary for laser experiments were checked, as a result, it turned out that some of them were not entirely correct. Our estimation of the lasing threshold using the literature data did not give a value comparable with the experimental data. The fact of high level activation in $CeF_3:Nd^{3+}$ crystals and the lack of a correct data on the laser properties of this diode-pumped crystal prompted us to the studies described in this paper.

Fluoride crystals generally have low thermo-optical distortion when pumped compared to oxide crystals [2]. This means that a good quality laser beam can be obtained very easily. In this regard, the $CeF_3:Nd^{3+}$ crystal with an oscillation wavelength of 1064 nm can be used as the active medium of the master oscillator in a diode-pumped MOPA system, in which an amplifier based on a YAG:Nd crystal will be used.

At present, there are only a few works in the literature devoted to the study of the spectroscopic and laser properties of the $CeF_3:Nd^{3+}$ crystal. Brief excerpts from some of them are given below.

The laser properties of the $CeF_3:Nd^{3+}$ crystal were first studied by J. R. O'Connor and W.A. Hargreaves [3]. Their brief note is devoted to the study of the UV energy lamp pumping transfer to the Nd^{3+} ions via the Ce^{3+} ions of the host matrix. The contribution of the transfer to increasing the efficiency of laser oscillation in this medium was studied. It should be noted, these studies carried out at a temperature of about 90 K and lasing was obtained at a single wavelength of 1063.8 nm only.

The first unpolarized spectroscopic properties of this crystal were studied in work [1]. The lasing under lamp pumping was obtained at room and liquid nitrogen temperatures. As well it also was tested a hypothesis of the efficiency of excitation energy transfer from the crystal matrix to the activator. As a result, the authors concluded that the transfer was ineffective.

In one of the last works [4] there was an attempt to carry out more detailed spectroscopic studies of $CeF_3:Nd^{3+}$ crystal. This paper presents

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polarized absorption and luminescence spectra. However, these spectra in both polarizations do not differ in the number of peaks and in their wavelength positions. Only some peaks differ in intensity. For crystals with an optical axis, this is unlikely. Based on the data obtained, an assessment was made of the prospects of the $CeF_3:Nd^{3+}$ crystal for obtaining two-wave laser oscillation in the region of one micron.

In paper [1] the plot of Nd^{3+} ions lifetime versus concentration in the $CeF_3:Nd^{3+}$ crystal drew our attention. This graph shows the concentration quenching of luminescence does not occur of the activator content of up to 4%. It only decreases from 300 μs at the low concentrations of Nd^{3+} ions to 280 μs at 4%. All this facts was a stimulus for a more thorough study of the $CeF_3:Nd^{3+}$ crystal properties as a promising diode-pumped active medium.

2. Samples

The space symmetry group of the $CeF_3:Nd^{3+}$ crystal has been reported in Ref. [1] as C6/mcm and then referring another work - as p3ci. The authors of this work assumed that CeF_3 and LaF_3 have the same structure. However, as shown in Ref. [5], published later, the structures of these crystals differ and the space symmetry group of the CeF_3 crystal is defined as *P*6$_3$*/mcm*.

$CeF_3:Nd^{3+}$ crystals were grown from melt by the Bridgman method in graphite crucibles in a fluorinating argon atmosphere (99.99%) at an excess pressure of 0.1–0.3 at. The CeF_3 crystal can be activated by Nd^{3+} ions up to a concentration of 4 at.% without the formation of visual defects. The CeF_3 crystal is anisotropic: it has an optical axis. Therefore, the grown boules were oriented using a polarizing microscope. Then samples were prepared from the boules for spectroscopic and laser studies.

3. Absorption spectra

The absorption spectra of the $CeF_3:Nd^{3+}$ crystal are given only in a few works. These spectra are represented either by individual narrow spectral regions, or in unpolarized light, or not quite correct. For example, the spectra given in Ref. [1] are presented only in a narrow spectral range and are not convenient for next analysis. Paper [3] presents not correct data on polarized absorption spectra. The spectra in this work in both polarizations practically do not differ. In paper [6], the absorption spectra are given in a wide range of the spectrum, but in unpolarized light.

The polarized absorption spectra of the $CeF_3:Nd^{3+}$ crystal recorded by us are shown in Fig. 1. A comparative analysis of the spectra shows

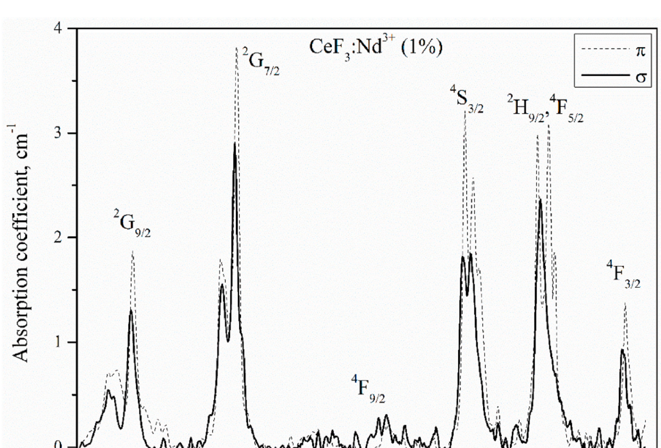

Fig. 1. Polarized absorption spectra of the $CeF_3:Nd^{3+}$ crystal.

their significant difference. The first thing to note is that the total intensity of the lines of the π - polarized spectrum is higher than the σ - polarized one. There is a difference between the line positions of the maxima in wavelengths in these spectra. In addition, we see the appearance of additional spectral lines. This difference is especially noticeable in part of the IR region of the spectra.

The maximum of the absorption line due to the $^4F_{3/2}$ term in the π-polarization (with a wavelength of 861.5 nm) is shifted to the short-wavelength side by three nm relative to this line in the σ-polarization with a wavelength of 858.5 nm. The lines of term $^2H_{9/2}$, $^4F_{5/2}$ represented in the σ-polarization by two Stark components (the long-wavelength one is weakly expressed), while in the π-polarization these lines consist of three allowed components. The $^4S_{3/2}$ term, judging by the spectrum, in the σ-polarization is also split into two components with wavelengths of 728 and 735 nm, while in the π-polarization this state is represented by three Stark components with wavelengths of 730.5, 736.5 and 741 nm. The remaining overlying states have smaller differences - they have a significant difference only in absorption intensities; the difference in wavelengths is no more than one nm.

The differences can be explained as follows. Optical centers of the activator in crystals with an optical axis are in an anisotropic crystal field. Therefore, depending on the orientation of the optical axis of the crystal relative to the observer, the Stark structure of its states differs. Accordingly, polarized light with a parallel or perpendicular orientation to the crystal axis is absorbed differently.

Thus, based on the presented spectra, we can find a suitable band for diode pumping of the $CeF_3:Nd^{3+}$ crystal. So, for the π-orientation the best absorption band is in the region of 800 nm, due to the $^2H_{9/2}$, $^4F_{5/2}$ states. Moreover, in our opinion, the most convenient band for pumping is 796.5 nm, which has a maximum absorption intensity and a half-width of about eight nm. In another orientation of the sample, the best choice for excitation of luminescence is the band with a maximum at 790 nm, the half-width of which is 11 nm. In both cases, the half-width of the selected absorption lines is much larger than the half-width of the emission band of a diode laser (usually about 3 nm). In this case, the requirements for pump wavelength stability will be low.

4. Spectra of luminescence

The luminescence spectra of the $CeF_3:Nd^{3+}$ crystal are presented in a number of works. In paper [1], the not polarized luminescence spectra recorded at room and nitrogen temperatures are presented. In paper [6], the luminescence spectra of $CeF_3:Nd^{3+}$ crystal samples with different concentrations of activator ions are presented, but the spectra are also unpolarized. An attempt was made in work [4] to record the polarized luminescence spectra of this crystal, but no difference was observed in the presented spectra.

The polarized luminescence spectra of the $CeF_3:Nd^{3+}$ crystal we recorded at room temperature. For excitation of the luminescence, a diode laser radiation with a wavelength of 797 nm was used. The spectra are shown in Fig. 2. These spectra were recorded using a StelarNet spectrometer and a Nicol prism. A source with a spectrum close to that of a black body was used to calibrate the transmittance function of the spectral setup.

Luminescence spectra of the $CeF_3:Nd^{3+}$ crystal are represented in Fig. 2 by two groups of lines in the region of 850–1100 nm. These groups of lines are due to inter-Stark transitions between terms. One of them is from the states of the $^4F_{3/2}$ term to the states of $^4I_{11/2}$ (1020–1100 nm). The next one is from - $^4F_{3/2}$ to $^4I_{9/2}$ (840–920 nm) - the Stark levels of the ground state. Two spectrally resolved lines at 1047 and 1063.5 nm represent the part of the spectrum due to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions in the σ polarization. Also, in the left side of the 1047 nm line, a part of the spectrally unresolved line in the region of 1037 nm is observed. While in π-polarization these transitions are represented by three spectrally resolved lines at 1063.5, 1046.5, and 1041 nm. Three spectrally resolved lines in both polarizations represent the part of the spectrum due to the

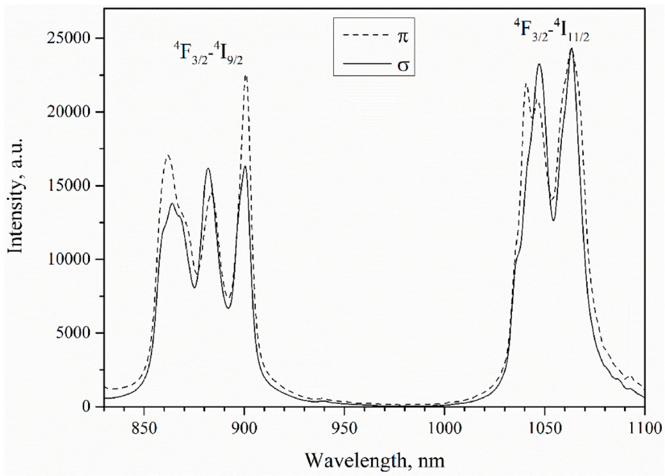

Fig. 2. Luminescence spectra of the CeF_3:Nd^{3+} crystal sample in different polarizations.

$^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions. But, there are some differences in the positions of their maxima and their structure. Thus, if the lines at 901 nm practically coincide in both polarizations, the maxima of the other two lines are shifted by 1.5–2 nm in different directions.

5. Luminescence lifetime vs concentration activator

We study the properties of the luminescence kinetics of the $^4F_{3/2}$ state of Nd^{3+} ions in a CeF_3 crystal as a function of the activator concentration. Two series of crystal samples with different degrees of activation were grown. The growing was carried out in a crucible with seven cavities. A mixture with different concentrations of the activator was placed in each of the cavities of the crucible. The first series of samples had the following concentrations of Nd^{3+} ions in the crystal: c = 1, 2, 3, 4, 5, 6, 7 at.%. On the preliminary plot, the inflection was in the region of 1–2% instead of the expected inflection in the region of 4% [1]. An additional series of crystals with different concentrations of activator was grown to refine the dependence. This series included concentrations of 0.1, 0.7, 1.3, 1.6, 2.3, 2.5, and 2.7 at. %. The luminescence kinetics of the samples had a predominantly single-exponential view. It is indirectly spoke of the single-center character of crystal activation. The final dependence of the luminescence lifetime of the CeF_3:Nd^{3+} crystal on the concentration of the activator is shown in Fig. 3. The diode laser radiation at the wavelength of 797 nm was used for excitation luminescence of CeF_3:Nd^{3+} crystal samples in all these experiments.

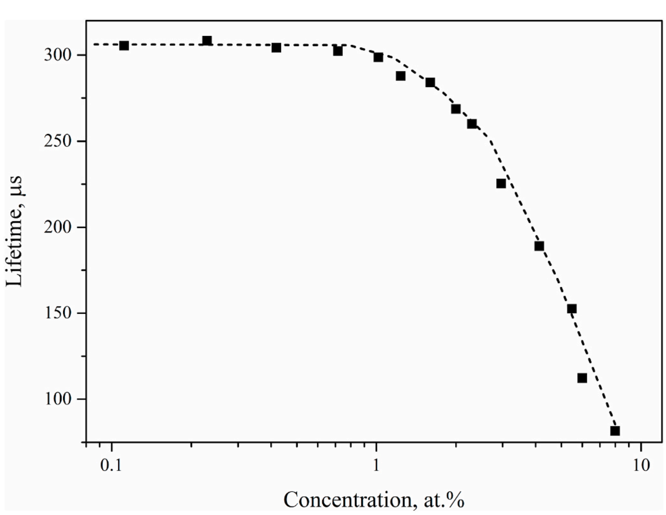

Fig. 3. Luminescence lifetime of the $^4F_{3/2}$ state of Nd^{3+} ions in a CeF_3 crystal versus activator concentration.

From the dependence shown in Fig. 3, we can estimate the radiative lifetime of the $^4F_{3/2}$ state of Nd^{3+} ions in the CeF_3 crystal, which is about 305 μs. The onset of concentration luminescence quenching is detected at a concentration of Nd^{3+} ions of 1–1.2 at.%. This parameter differs significantly from that presented in Ref. [1]. The value of this parameter for CeF_3:Nd^{3+} crystal is the same as for most fluoride crystals and glasses [7–10].

6. Estimation of the lasing threshold

Based on the obtained values of the spectroscopic data of the CeF_3:Nd^{3+} crystal, we have estimated the threshold of possible lasing. For this estimate, we used the formula proposed in the work [11]:

$$p = \frac{8\pi\tau_s\nu_0^2}{c^3 g(\nu)\tau_p} \cdot \frac{h\nu_e}{\eta} \quad (1)$$

where τ_s is the fluorescence lifetime of the sample, in our case, the fluorescence lifetime of the $^4F_{3/2}$ level of the Nd^{3+} ion; τ_p is the lifetime of generated photons in the cavity; ν_0 is the emission frequency of the maximum of the most intense luminescence line; $h\nu_e$, c, η are the pump photon energy, speed of light, and luminescence quantum yield, respectively; $g(\nu)$ is the form factor, which for the Lorentzian profile of spectral lines is determined by the expression:

$$g(\nu) = \frac{2}{\pi.\Delta\nu} \quad (2)$$

where $\Delta\nu$ is the half-width of the luminescence line of the most intense line. The lifetime of generated photons in the cavity is defined as [12]:

$$\tau_p = 2.\frac{L}{c}.(-\log(R_1.R_2) + 2.\delta.l)^{-1} \quad (3)$$

δ is the coefficient of inactive losses of the active medium, c, l, L are the speed of light, length of the active medium, and length of the cavity, respectively.

In our case, the luminescence lines were quite reliably described by the Lorentz function. The lifetime of the $^4F_{3/2}$ state of the Nd^{3+} ion is 305 μs. Pumping was assumed to be carried out at a wavelength of 797 nm. Laser oscillation was expected at a wavelength of 1064 nm. The part of the luminescence quantum yield [13] attributable to the most intense line of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition at a wavelength of 1064 nm was estimated at 0.21. As a result of calculations using all the obtained spectroscopy data, the threshold value of the pump energy was found to be 2.3 mJ. It should be kept in mind that the calculations did not take into account the narrow directivity of the oscillated radiation. Also, it takes into account the pumping efficiency, and the fact that expression 3 was derived from the condition of oscillation of an infinitely narrow laser line, which is usually not fulfilled in practice.

7. Laser experiments

For experiments on the study of laser properties, two pairs of active elements (AE) were fabricated with an activator ion concentration of 1 and 2%. The AE were parallelepipeds 2.7 × 7 × 10 mm (h, d, l) in size (See Fig. 4).

An optical axis in both AE was normal to l, d planes. In laser experiments, the AE were placed by dimension l along the axis of the cavity. The optical axis of AE - C was oriented normal to axis of the cavity. A dichroic end cavity mirror (ECM) of a cavity coupler with a radius of curvature r = 700 mm was rigidly connected in a block with a lens. The laser diode with a wavelength of 797 nm was used for pumping of CeF_3:Nd^{3+} crystal samples. The radiation of the laser diode was compensated along the slow axis by a cylindrical lens with a focal length f = 180 mm (does not shown on picture). The lens was installed at a

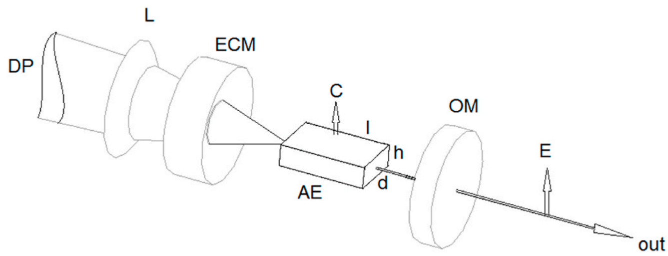

Fig. 4. Experimental laser setup.

distance of 150 mm from the lens that focused the radiation onto the active element. The lens - L with a focal length f = 25 mm focused the pump radiation onto the sample. As a result, the radiation spot at the end of the AE had dimensions of about 0.3 mm in diameter. Output couplers with a flat surface and different reflection coefficients (0.995, 0.990, 0.985) were alternately replaced in the experiments. A laser diode was used to pump the samples of the CeF_3:Nd^{3+} crystal. Its pulse duration and the repetition rate were 1 ms and 50 Hz, respectively.

The lasing at the AE was obtained by scanning the h, d plane of the AE with the pump spot to find the best lasing channel. A polarization of the laser radiation was always parallel to the optical axis of AE independent on orientation of AE in cavity and the pumping radiation polarization. The lasing was obtained at wavelength of 1064 nm only (See Fig. 5). Nevertheless, in work [1], with lamp pumping, lasing was obtained not only at a wavelength of 1063.8 nm, but also at 1041 nm. It can be assumed, by analogy with $LiYF_4$:Nd^{3+}, that if the optical axis of the CeF_3:Nd^{3+} AE passes along the cavity axis, then the laser radiation wavelength will change. This assumption will be considered in our next work.

The results of measurement of energy characteristics of laser oscillation at 1064 nm are shown on Fig. 6. The most slope efficiency of 25.2% was obtained using an output coupler with a reflectance of 0.985, at which the threshold energy was no more than 0.4 mJ. The lasing threshold determined in experiments turned out to be less than the value obtained as a result of theoretical estimates.

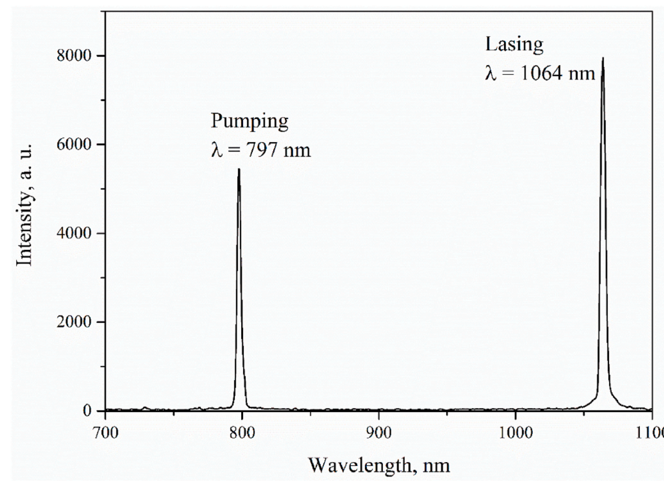

Fig. 5. Pumping laser and laser oscillation of CeF_3:Nd^{3+} crystal spectra.

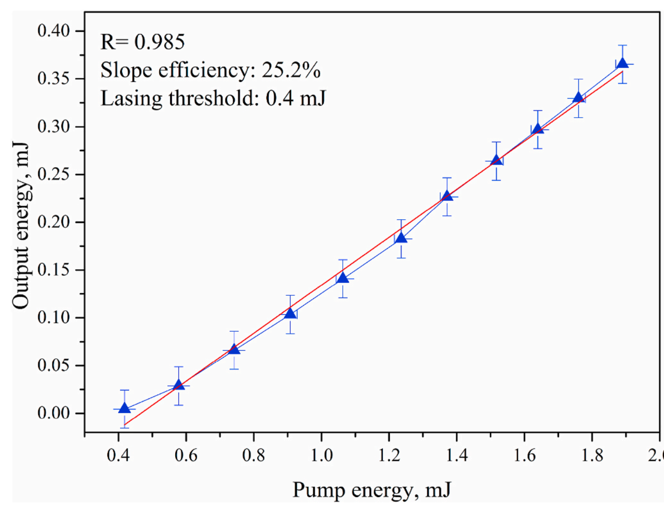

Fig. 6. Oscillation energy of CeF_3:Nd^{3+} crystal versus pump energy for output coupler with reflectance of 0.985.

8. Conclusion

As a result of this work, the polarizing spectroscopic properties of the CeF_3:Nd^{3+} crystal were corrected and supplemented. The concentration dependence of lifetimes of luminescence conditioned by the transitions $^4F_{3/2}$ - $^4I_{11/2}$ in the crystal was measured more thoroughly using fourteen samples with different concentrations. According to this dependence, quenching in the crystal differs sharply from the data presented in the literature. So the CeF_3:Nd^{3+} crystal has luminescence quenching, which is typical for most fluoride crystals and which occurs at a concentration of 1–1.5% of the activator ions. Based on the corrected data on the spectroscopic properties, the attainment of the lasing threshold on CeF_3:Nd^{3+} crystal is quantitatively estimated.

The first experiments on obtaining lasing on a CeF_3:Nd^{3+} crystal with diode pumping was carried out with only a samples which has optical axis normal to the l, d side. As the result we have got laser oscillation only at one wavelength - 1064 nm. Lasing at a different wavelength may require a sample with optical axis along the l edge of crystal body and parallel to the cavity axis. The lasing threshold reached is in good agreement with the theoretical estimate. Experimental dependences of the output energy of laser oscillation on CeF_3:Nd^{3+}crystal with diode pumping with different reflection values of the output coupler are obtained. A slope efficiency of 25.2% was reached with the output coupler R = 0.985.

Authorship contribution statement

Alexander **Naumov**: Conceptualization, Validation, Methodology, Software, Writing - Review & Editing, Supervision, contribute equally. **Radik Aglyamov:** Investigation, Formal analysis, Writing- Original draft preparation, contribute equally.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Naumov A.K. reports financial support was provided by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities No. FZSM-2020-005. Aglyamov R.D. reports financial support was provided by the government assignment for FRC Kazan Scientific Center of RAS (theme No AAAA-A19-119011790156-3).

Data availability

Data will be made available on request.

Acknowledgments

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