

and Dy_2O_3 have cubic structure up to 1473° and $2423^\circ K$, respectively. Above these temperatures Gd_2O_3 and Dy_2O_3 possess monoclinic structure. Thus, the magnetic susceptibility studies of Gd_2O_3 and Dy_2O_3 presented in this paper are for the cubic phase.

ACKNOWLEDGMENTS

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Optical Maser Emission from Trivalent Praseodymium in Calcium Tungstate*

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Coherent emission at 1.047μ from trivalent praseodymium in calcium tungstate was observed. This emission coincides with strong infrared fluorescence at the same wavelength and was found to be stimulated mostly by absorption of blue light by the 3P_0 , 3P_1 , and 3P_2 bands. The emission corresponds to a $^1G_4 \rightarrow ^3H_4$ transition with the terminal level 377 cm^{-1} from the ground state. The oscillation threshold was the same at 4.2° , 20° , and $78^\circ K$. No stimulated emission was observed at room temperature. The lifetime of the metastable state 1G_4 is 50×10^{-8} sec. A new technique used to measure the lifetime is described.

I. INTRODUCTION

THE small electrostatic energy of the rare-earth ions in crystalline electric fields endows them with narrow linewidth fluorescences originating in metastable states whose lifetime is often radiative.¹ These properties, when coupled with the existence of absorption bands in the visible and near visible region which are coupled strongly to the metastable state are among the main prerequisites for optical maser materials.²

Two rare-earth elements³ already shown as optical maser additives are Sm^{++4} and Nd^{3+} .⁵ We have observed stimulated emission from trivalent praseodymium in calcium tungstate ($CaWO_4:Pr^{3+}$) at 1.0468μ which is stimulated by the absorption of blue light with a relatively low threshold.

II. THE ENERGY LEVELS

In Fig. 1 are shown the positions of the main energy levels of Pr^{3+} which are reproduced from the work of Dieke and Sarup.⁶ The levels are those of Pr^{3+} in $PrCl_3$, but since the stark splitting is not shown they correspond very closely to the levels in $CaWO_4$. A more

detailed diagram showing only those levels pertinent to the understanding of the operation of the maser is shown in Fig. 2. The energy absorption from the pump light induces transitions from the ground state into the 3P_0 , 3P_1 , and 3P_2 levels. These absorption bands are shown in Fig. 3. The excitation is next transferred to the metastable state which belongs to the stark-split 1G_4 level and which lies 9930 cm^{-1} above the ground state. The coherent emission corresponds to a transition at 1.0468μ (9553 cm^{-1}) from the metastable state to a level at 377 cm^{-1} from the ground state belonging to 3H_4 .

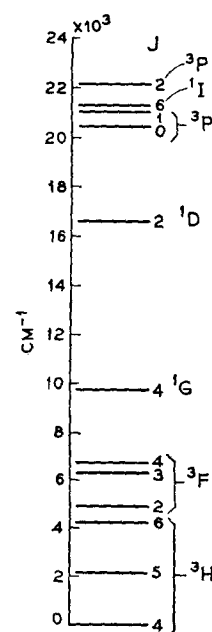


FIG. 1. The energy levels of Pr^{3+} in $PrCl_3$. No stark splitting is shown. The diagram is reproduced from a paper by Dieke and Sarup.⁶

* Some of the material included in this paper was presented in a post deadline paper at the Northeast Electronics Research and Engineering Meeting, November 1961.

¹ G. H. Dieke and L. A. Hall, *J. Chem. Phys.* **27**, 467 (1957).

² A. L. Schawlow and C. H. Townes, *Phys. Rev.* **29**, 1940 (1958).

³ Since the influence of the host crystal on the rare-earth ion is of secondary importance as far as the energy levels are concerned we refer to the maser material by the name of the ion.

⁴ P. P. Sorokin and M. J. Stevenson, *Phys. Rev. Letters* **5**, 557 (1960).

⁵ L. F. Johnson and K. Nassau, *Bull. Am. Phys. Soc.* **6**, 414 (1961).

⁶ G. H. Dieke and R. Sarup, *J. Chem. Phys.* **29**, 741 (1958).

The three absorption bands are responsible for the light green tint of the crystal for Pr^{3+} concentrations above 0.05%. The ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ transition has a width of $\approx 70 \text{ cm}^{-1}$ and an oscillator strength f , as measured from the integrated absorption, of $\approx 2 \times 10^{-5}$. The ${}^3\text{H}_4 \rightarrow {}^3\text{P}_0$, ${}^3\text{P}_1$ transitions have, each, a width of $\approx 50 \text{ cm}^{-1}$ and an oscillator strength of $\approx 10^{-5}$. The separation of the terminal level from the ground state (377 cm^{-1}) qualifies the material as a four-level maser at temperatures below 100°K . At these temperatures the population of the terminal level is small in comparison to the critical (at threshold) population inversion and the terminal level may be considered "empty."

III. THE OPTICAL MASER EXPERIMENTS

The coherent emission was observed from a crystal of 0.5 mole-percent Pr in CaWO_4 , 3.6 cm long and 0.3 cm in diameter. The two end faces were ground into spherical surfaces with a radius of 3.6 cm so as to form a confocal resonator.⁷ One side was silvered for no transmission in the visible while the other surface was left slightly (2%) transmissive.

The crystal was submerged in a variety of cryogenic fluids in the manner depicted by Fig. 4. The excitation was provided by a FT-524 Xe flash lamp which surrounded the crystal. The stimulated emission at 1.0468μ was detected by a type 7102 RCA photomultiplier.

The oscillation threshold for the arrangement described above was $\approx 20 \text{ J}$ at 20° , 77° , and 90°K . No oscillation was observed at room temperature with energy inputs of up to 2000 J. This is consistent with the separation of the terminal level from the ground state which is 377 cm^{-1} .

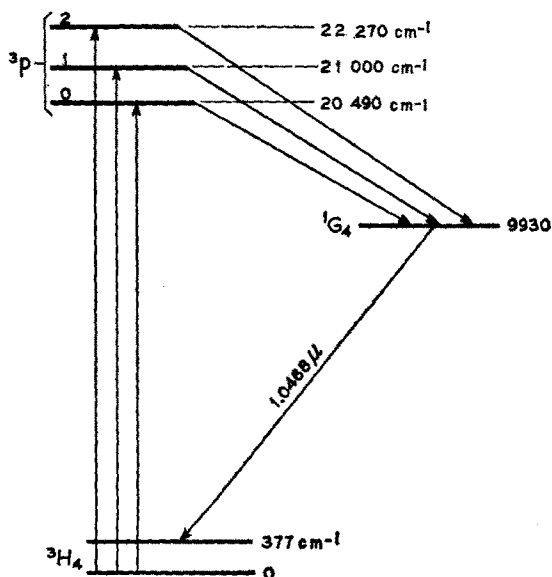


FIG. 2. Energy level diagram for levels partaking directly in maser action in $\text{CaWO}_4:\text{Pr}^{3+}$.

⁷ G. D. Boyd and J. P. Gordon, Bell System Tech. J. 40, 489 (1961).

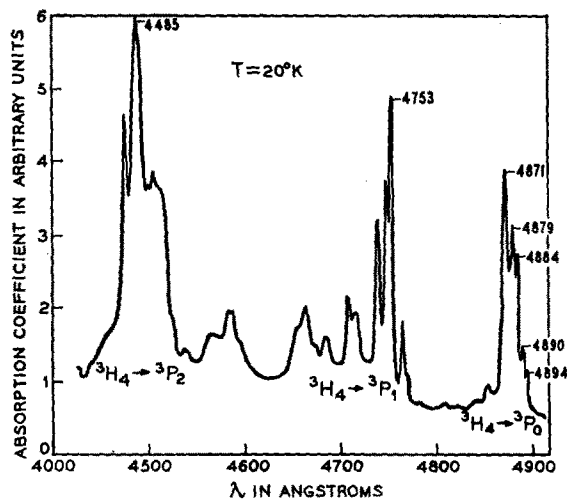


FIG. 3. The absorption curve for the ${}^3\text{H}_4 \rightarrow {}^3\text{P}_{0,1,2}$ transitions.

By placing the flash lamp just alongside the crystal-containing Dewar and using sharp cutoff Corning filters between the lamp and the Dewar it was possible to ascertain that the stimulated emission was induced primarily by absorption in the three blue bands discussed above.

Figure 5 shows the oscillation output with the now familiar modulation pattern. This picture was obtained with the maser beam focused on the entrance slit of a Perkin-Elmer type 210 grating monochromator and with the photomultiplier at the exit slit.

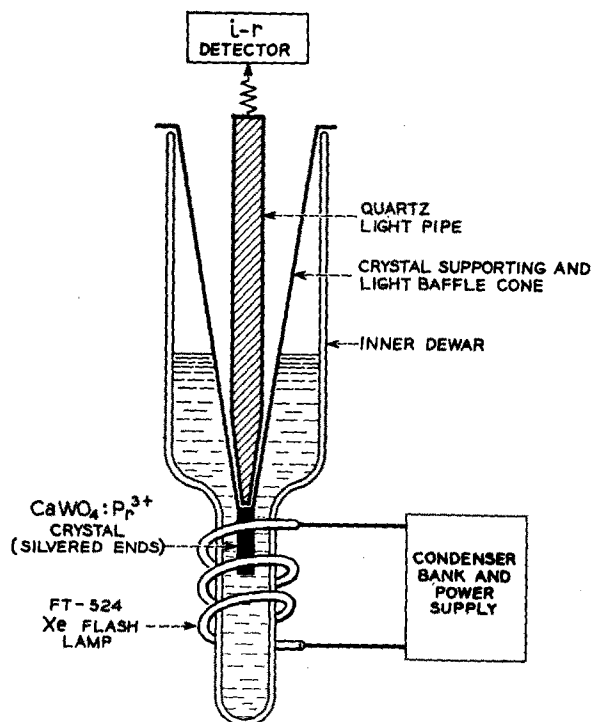


FIG. 4. The experimental setup.

IV. THE LIFETIME MEASUREMENT

The conventional method for measuring the lifetime of the metastable state involves excitation of the fluorescence by a sharp light pulse and a subsequent monitoring of the decaying fluorescence.

This technique becomes difficult for the case of weak fluorescence and weakly absorbing material which is the case with Pr^{3+} in CaWO_4 . We have overcome these difficulties by taking advantage of the intimate connection between the lifetime and the oscillation threshold. The measurement is based on the following considerations. If we assume that the relaxation time connecting the absorption bands ($^3P_0, ^3P_1, ^3P_2$) and the metastable state as well as the lifetime of the terminal level are all short in comparison to the lifetime τ of the metastable state, we can show that the population N of the metastable state obeys the following differential equation

$$dN/dt = aP - (N/\tau), \quad (1)$$

where P is the instantaneous energy density (in the wavelength region absorbed by the blue bands) and a is a proportionality constant whose numerical value is not needed. Oscillation starts as soon as N reaches a critical value N_c which depends on the photon lifetime and the transition probability per photon per mode.² If we now consider a parallel RC circuit fed by a current generator $i(t)$, the voltage V across the network obeys

$$dV/dt = [i(t)/C] - (V/RC). \quad (2)$$

A comparison of Eqs. (1) and (2) reveals that if we can make $i \propto P$ and $\tau = RC$ there will exist a one-to-one correspondence (and one of direct proportionality) between the voltage V and the excess population N . At the instant at which oscillation starts we should thus have the same voltage V_c across the network, one corresponding to N_c .

The experimental procedure consists of the normal maser experiment with the addition of a phototube which samples the pumping light (from the FT-524)

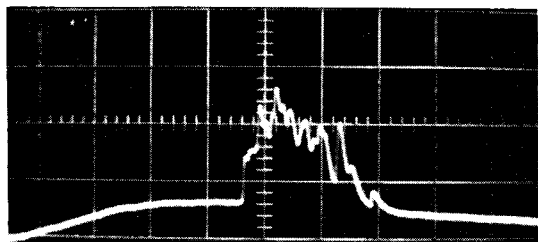


FIG. 5. The oscillation output at 1.0468μ . The horizontal scale is $50 \mu\text{sec}/\text{div}$.

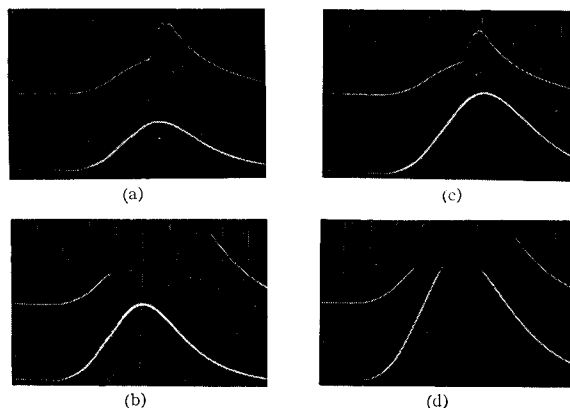


FIG. 6. Measurement of the lifetime of the 1G_4 level of $\text{CaWO}_4:\text{Pr}^{3+}$ at 77°K . (a): $RC = \tau = 50 \mu\text{sec}$, energy input = 40 J, (b): $RC = \tau = 50 \mu\text{sec}$, energy input = 60 J, (c): $RC = 2\tau = 100 \mu\text{sec}$, energy input = 40 J, (d): $RC = 2\tau = 100 \mu\text{sec}$, energy input = 60 J.

and drives an RC network with a current instantaneously proportional to P . The voltage across the RC network is displayed simultaneously with the output from the 7102 photomultiplier on a dual beam scope and the voltage at threshold is noted. For a given RC setting we excite the oscillation with a number of energy inputs until we find a setting for which the output voltage at start oscillation is independent of the pump energy. For this setting $RC = \tau$. The lifetime at 77°K as measured by this technique is $\tau = 50 \times 10^{-6} \text{ sec} \pm 5 \times 10^{-6} \text{ sec}$. In Figs. 6(a)–6(d) we see the results obtained with $RC = 50 \times 10^{-6} \text{ sec}$ and with $RC = 100 \times 10^{-6} \text{ sec}$.

V. OSCILLATION THRESHOLD

The most fundamental quantity with which to characterize the threshold of a given maser material is its critical population inversion per unit volume in an optical resonator of a given quality factor (Q). A quantity directly related to the critical population inversion and one more accessible to measurement is the incident energy flux in watts/cm^2 at the crystal surface at threshold, where only energy useful in stimulating fluorescence is considered. A method for comparing thresholds is to measure the energy input, at threshold, to a given flash lamp in a given excitation geometry. Using the last criterion, the threshold energy for a 0.5% Pr in CaWO_4 at $T < 91^\circ\text{K}$ is 20 J for a crystal silvered to opacity on one side and to 2% transmission on the other and which is placed at the center of a FT-524 Xe flash lamp. The energy flux under this condition is $1\text{--}2 \text{ W}/\text{cm}^2$ for energy within the absorption bands.