the order of one their expression may be written

$$\Delta E_g = \frac{-\pi(e^*e)^2}{\Omega M\omega^{3/2}}\left[\left(\frac{2m_e^*}{\hbar^2}\right)^{1/2}+\left(\frac{2m_h^*}{\hbar^2}\right)^{1/2}\right](n+1),$$

where $n=1/[(\exp\hbar\omega/kT)-1]$, ω is the angular frequency of the longitudinal optical phonon, Ω is the volume of the unit cell, M is the reduced mass of the atoms, e^* is the effective ionic charge, and m_e^* and m_h^* are the effective masses of the charge carriers in the conduction and valence bands, respectively. For CdS, $\omega=0.58\times10^{14}$,[19] $e^*=0.72$,[20] $m_e^*=0.7\ m_e$, and $m_h=0.2\ m_e$ and $5.0\ m_e$,[8] parallel and perpendicular to the c axis, respectively. Using these values the solid curve in Fig. 3 is plotted. The experimental data are plotted as the circles. While at high temperatures the theoretical curve is somewhat in agreement with the experimental values, at low temperatures the agreement is not satisfactory. However, the validity of applying the theory of Fan and Radkowsky to a material where the effective mass is large is somewhat doubtful. There is also the probability that there are piezoelectrically active acoustical modes which are important below 150°K.[21] This has been pointed out by Piper, Johnson, and Marple[22] to explain the failure of the theory to account for the temperature dependence of the band gap in ZnS in the region below 150°K.

[19] R. J. Collins, J. Appl. Phys. **30**, 1135 (1959).
[20] F. Keffer, J. Chem. Phys. **33**, 1267 (1960).
[21] H. J. G. Meijer and D. Polder, Physica **19**, 225 (1953).
[22] W. W. Piper, P. O. Johnson, and D. T. F. Marple, J. Phys. Chem. Solids **8**, 457 (1959).

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Maser Oscillations at 0.9 and 1.35 Microns in $CaWO_4$:Nd^{3+}

L. F. Johnson and R. A. Thomas
Bell Telephone Laboratories, Murray Hill, New Jersey
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Previous reports have described optical maser oscillation at $\sim$1.06 μ from Nd^{3+} in $CaWO_4$. Oscillation occurs in $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transitions, the terminal state lying $\sim$2000 cm^{-1} above the ground state. The present note reports maser oscillation in $^4F_{3/2}\rightarrow{}^4I_{13/2}$ transitions, the terminal states lying $\sim$4000 cm^{-1} above the ground state, and in $^4F_{3/2}\rightarrow{}^4I_{9/2}$ transitions, the terminal state lying 471 cm^{-1} above the ground state. Attempts to obtain maser oscillation at $\sim$5 μ in transitions between ^4I multiplets were unsuccessful. It is concluded that these transitions are predominantly nonradiative.

INTRODUCTION

PREVIOUS publications[1–3] have described details of optical maser oscillation at $\sim$1.06μ arising from $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transitions of Nd^{3+} in $CaWO_4$. The terminal state for these transitions, $^4I_{11/2}$, lies $\sim$2000 cm^{-1} above the ground state. The present note reports maser oscillation in $^4F_{3/2}\rightarrow{}^4I_{13/2}$ transitions, the terminal states lying $\sim$4000 cm^{-1} above the ground state, and in $^4F_{3/2}\rightarrow{}^4I_{9/2}$ transitions, the terminal state lying 471 cm^{-1} above the ground state.

When irradiated by white light, the trivalent neodymium ion in $CaWO_4$ produces strong infrared fluorescence consisting of three groups of lines centered at 0.9, 1.06, and 1.35μ. The emission corresponds, respectively, to transitions from $^4F_{3/2}$ to the $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ multiplets of the ground term. Since for all transitions the σ spectrum (E vector perpendicular to c axis) coincides with the axial spectrum (emitted beam parallel to c axis), the transitions are electric dipole. The strongest emission, preferred for maser oscillation, is $^4F_{3/2}\rightarrow{}^4I_{11/2}$, but with selective feedback by means of multiple layer dielectric reflectors, oscillation may be obtained in transitions to either $^4I_{13/2}$ or $^4I_{9/2}$.

[1] L. F. Johnson and K. Nassau, Proc. I.R.E. **49**, 1704 (1961).
[2] L. F. Johnson, G. D. Boyd, K. Nassau and R. R. Soden, Phys. Rev. **126**, 1406 (1962).
[3] L. F. Johnson, J. Appl. Phys. (to be published); Quantum Electronics Conference, Paris, 1963 (to be published).

$^4F_{3/2}\rightarrow{}^4I_{13/2}$ TRANSITIONS

The polarization of the $^4F_{3/2}\rightarrow{}^4I_{13/2}$ emission (Na^+ compensation) is shown in Fig. 1. Maser transitions and their threshold energies (as measured by the electrical input to an FT 524 xenon lamp) are indicated in the figure. At room temperature, maser oscillation is obtained in the π line at 1.339μ (7467 cm^{-1}). At 77°K, oscillation is observed in three lines at 1.337μ (7478 cm^{-1}), 1.345μ (7435 cm^{-1}), and 1.387μ (7210 cm^{-1}). The low-threshold line at 1.337μ has a width of 6.4 cm^{-1} at 77°K and 2.4 cm^{-1} at 20°K. The line at 1.345μ is of about equal intensity, but has a width of 6.9 cm^{-1} at 77°K and 3.3 cm^{-1} at 20°K; therefore, oscillation occurs at a slightly higher threshold.

With the aid of absorption data, an energy level diagram identifying the $^4F_{3/2}\rightarrow{}^4I_{13/2}$ transitions and their polarization is derived in Fig. 2. Several lines seen in fluorescence (Fig. 1) are believed to be satellites and are not included in Fig. 2. The location of six of the seven crystal field components of $^4I_{13/2}$ has been determined. At 295°K, the initial state for the maser line is the upper component of $^4F_{3/2}$, the terminal state lying 4004 cm^{-1} above the ground state. Maser oscillation is not observed in this line at 77°K due to a reduced Boltzmann factor. At 77°K, three maser lines originate from the lower component of $^4F_{3/2}$. The terminal state for the line of lowest threshold lies 3928 cm^{-1} above the ground state. Oscillation is not observed at 77°K between the lower component of $^4F_{3/2}$ and the terminal state for the maser line at room temperature, due to the fact that this transition is very weak and broad (line E in Fig. 1).

The lines of lowest threshold at 295 and 77°K both possess π polarization, in contrast to the polarization character of the low-threshold lines at 1.06μ (σ polarization at 77°K; π polarization at 295°K).[3] The threshold of 3.6 J at 1.34μ at 295°K is to be compared with a threshold of 2.1 J for the same resonator at 1.06μ. Reduction of threshold experiments[2] indicates that with small improvements continuous operation at 1.34μ is possible.

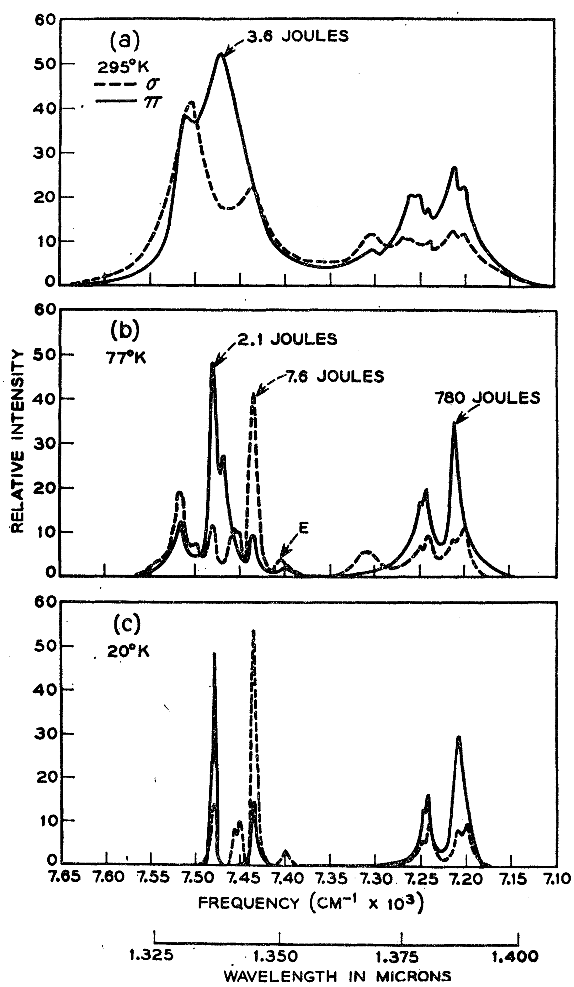

FIG. 1. Polarization of the $^4F_{3/2} \rightarrow {}^4I_{13/2}$ emission in $CaWO_4$:Nd^{3+} (Na^+ compensation) at 295, 77, and 20°K. Maser lines and threshold energies measured in an FT 524 xenon lamp are designated.

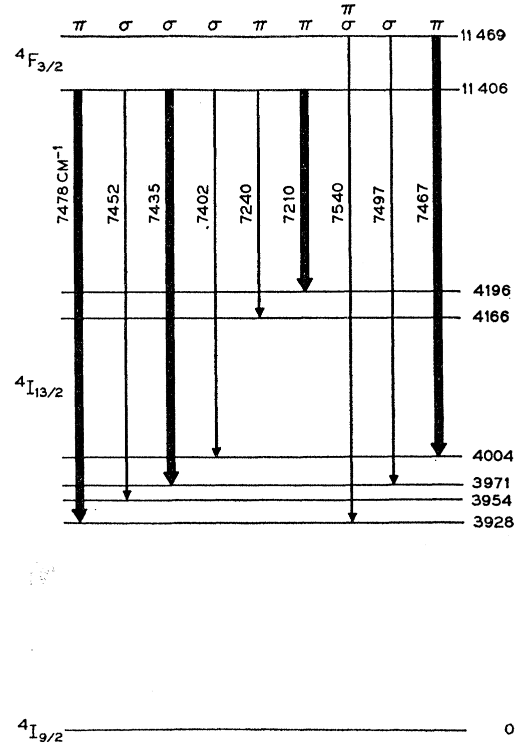

FIG. 2. Energy levels of $^4F_{3/2}$ and $^4I_{13/2}$ multiplets of Nd^{3+} in $CaWO_4$ (Na^+ compensation). Maser transitions are indicated by heavy arrows.

$^4F_{3/2} \rightarrow {}^4I_{9/2}$ TRANSITIONS

Polarization spectra of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions are shown in Fig. 3. At 77°K stimulated emission is observed in the σ line at 0.9145μ (10 935 cm^{-1}), the terminal state lying 471 cm^{-1} above the ground state.[4] The width of this line in fluorescence is 15 cm^{-1} at 77°K

TABLE I. Summary of optical maser characteristics of Nd^{3+} in $CaWO_4$.

Transition	Temp (°K)	Maser wave-length (μ)	ν (cm^{-1})	Polarization	Threshold FT 524 (J)
$^4F_{3/2} \rightarrow {}^4I_{9/2}$	77	0.9145	10 935	σ	4.6
$^4F_{3/2} \rightarrow {}^4I_{11/2}$	77	1.0641	9398	σ^a	7
		1.0650	9390	σ	0.8
		1.066	9381	σ^a	6
	295	1.0582	9450	π	1.6
		1.0652	9388	σ	3
$^4F_{3/2} \rightarrow {}^4I_{13/2}$	77	1.3372	7478	π	2.1
		1.345	7435	σ	7.6
		1.387	7210	π	780
	295	1.3392	7467	π	3.6

[a] Satellite.

[4] Stimulated emission has previously been observed in this region from Nd^{3+} in glass [R. D. Maurer, Appl. Opt. 2, 87 (1963)].

and 11 cm^{-1} at 20°K. The five crystal-field components of $^4I_{9/2}$ are shown in Fig. 4. There is some uncertainty in the exact location of the level at 114 cm^{-1} due to weak, broad lines in absorption and emission, and the presence of nearby satellites. Maser oscillation is not observed at room temperature, due to thermal population of the $^4I_{9/2}$ levels. The threshold of 4.6 J at 0.9145μ at 77°K is to be compared with a threshold of 0.8 J for the same resonator at 1.065μ (77°K). It will be more difficult to achieve continuous operation at this wavelength.

A table summarizing the optical maser characteristics of Nd^{3+} in $CaWO_4$, including previously published data at 1.06μ,[3] is presented in Table I.

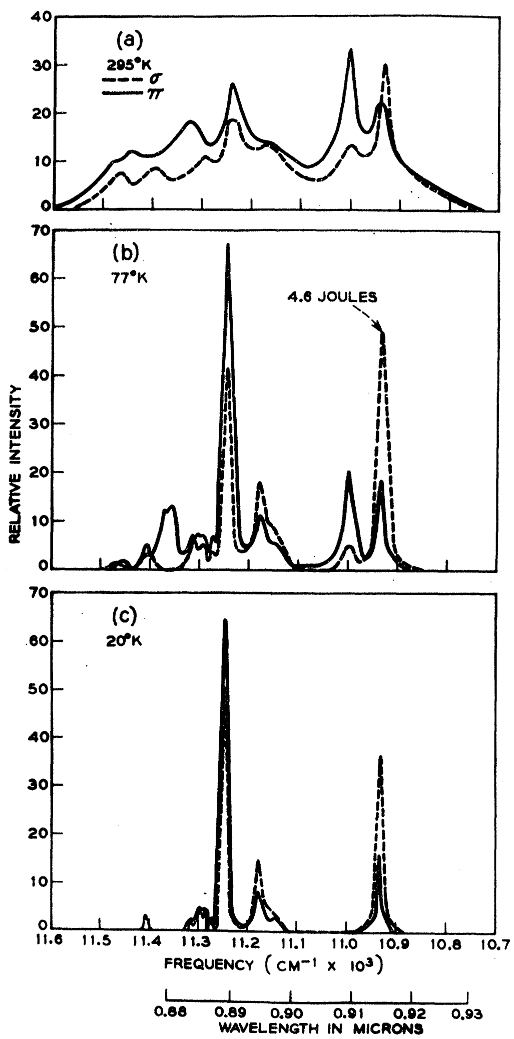

FIG. 3. Polarization of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission in $CaWO_4$:Nd^{3+} (Na^+ compensation) at 295, 77, and 20°K. Maser oscillation is observed at 77°K in the line at 0.9145μ (10 935 cm^{-1}).

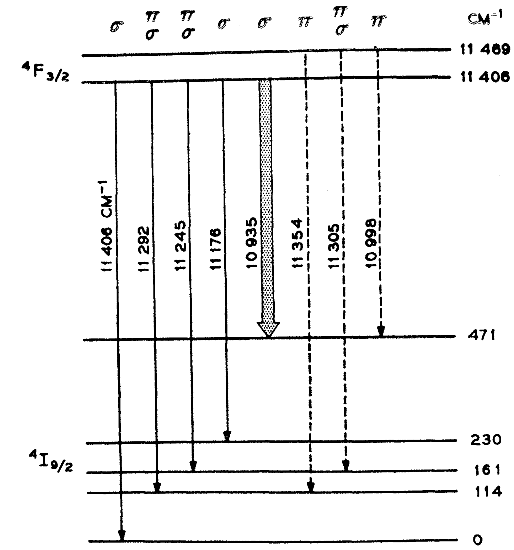

FIG. 4. Energy levels of $^4F_{3/2}$ and $^4I_{9/2}$ multiplets. The maser line terminates 471 cm^{-1} above the ground state. Dashed lines indicate additional transitions seen at 77°K.

Two attempts were also made, unsuccessfully, to produce stimulated emission in Nd^{3+} in the region 5–7 μ arising from transitions between ^4I multiplets: $^4I_{13/2} \rightarrow {}^4I_{11/2}$ and $^4I_{11/2} \rightarrow {}^4I_{9/2}$. In the first, dielectric coatings consisting of alternate layers of germanium and thorium oxyfluoride ($ThOF_2$) were applied to the end surfaces to produce a broad region of high reflectivity in the region 4–6μ (corresponding to the separation between both pairs of multiplets). In the second, silver reflectors were employed, one end being left partially transmitting ($\sim$5% at 1.06μ); the objective was to obtain inversion between $^4I_{11/2}$ and $^4I_{9/2}$ by means of the self-pumping action produced by stimulated emission to $^4I_{11/2}$. The experiments were carried out with Nd^{3+} in $CaWO_4$, CaF_2, and LaF_3 at 77 and 20°K (CaF_2 and LaF_3, unlike $CaWO_4$, do not possess lattice absorption in the region 5–7μ). We conclude from the failure of the experiments that transitions between the ^4I multiplets are predominantly nonradiative. This is supported further by a separate experiment in which little or no fluorescence was observed under pulse illumination conditions when the reflecting layers were removed from the end surfaces.

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