Laser Transition Cross Section and Fluorescence Branching Ratio for Nd^{3+} in Yttrium Aluminum Garnet

TAKASHI KUSHIDA, H. M. MARCOS, AND J. E. GEUSIC

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 6 November 1967)

The emission cross section at the laser line peak of YAlG:Nd^{3+} was measured at room temperature by two independent methods. The effective cross section for the ion in the upper (R_2) level of the $^4F_{3/2}$ manifold was found to be $(8.8\pm1.0)\times10^{-19}$ cm^2. The values determined by the two different methods agreed with each other within experimental error. The result indicates that nonradiative transitions from the emitting state are negligible compared with the radiative transitions. The measured fluorescence branching ratios are also presented.

INTRODUCTION

RECENTLY, optical refrigeration in yttrium aluminum garnet doped with neodymium (YAlG:Nd^{3+}) has been suggested by Geusic, Schulz-DuBois, and Scovil.[1] For the estimation of this process, we need such data as the transition cross section, fluorescence branching ratio, and the contribution of nonradiative transitions to the fluorescence decay time. This paper reports measurements of these properties for Nd^{3+} in YAlG at room temperature. YAlG:Nd^{3+} is an extremely useful laser material, and these data are important also from the standpoint of laser applications.

A measurement of the laser transition cross section for Nd^{3+} in YAlG has recently been reported by Neeland and Evtuhov.[2] They obtained the values of 2.7×10^{-19} and 3.5×10^{-19} cm^2 by two methods at room temperature. They ascribed the difference to the $^4F_{3/2}\rightarrow{}^4I_{13/2}$, $^4I_{15/2}$ emissions and nonradiative transitions which were neglected in the determination of the latter value. The magnitude of the cross section that they reported, as well as their experimental values such as the linewidth and absorption cross section, disagreed with previous unpublished measurements[3] beyond the limits of experimental error. To resolve this disagreement, we have made similar but more accurate measurements of the laser transition cross section, in addition to the branching ratio for the transitions from the emitting state in YAlG:Nd^{3+}.

The cross section at the peak of the laser line (1.0641 μ)[4] was determined at room temperature by the two methods which were also employed by Neeland and Evtuhov; namely, one method is to use the absorption cross section for the transition from the ground state to the emitting state and the ratio of the emission intensity of the inverse process to that of the laser transition, and the other is to deduce the cross section from the radiative transition probability determined from the branching ratio and the fluorescence decay time. In the latter method, we took into account the $^4F_{3/2}\rightarrow{}^4I_{13/2}$ and $^4I_{15/2}$ transitions which were not included in the determination of the branching ratio by Neeland and Evtuhov. We considered also the overlapping of two transitions in the laser line. The values determined by the two methods agreed with each other within experimental error. These new measurements indicate that the contribution of nonradiative transitions to the fluorescence decay time is negligible and give a laser transition cross section which is greater than twice that reported by Neeland and Evtuhov.

EXPERIMENTAL DETAILS

Specimens used were a slab (2 mm thick) and a cylindrical rod (2.5 mm in diameter, 13 mm long) which contained nominally 1 atomic percent of Nd ions. A part of the slab was chemically analyzed, and the Nd^{3+} concentration was found to be 1.0 (±0.1) atomic percent corresponding to the ground-state population density of 6.0×10^{19} cm^{-3} at room temperature.

The emission spectrum was determined in the spectral range from 0.77 to 2.1 μ using a Jarrell-Ash 1-m Ebert scanning spectrometer with a 15 000-line/in. grating blazed for 2 μ. In the 0.77- to 1.13-μ region, a high-pressure Osram HBO 500-W mercury lamp was used for the excitation, and the fluorescence was detected with a cooled RCA 7102 photomultiplier. A Corning glass color filter CS4-97 was inserted between the lamp and the specimen to prevent the scattered excitation light from reaching the detector. The fluorescence from the specimen in the 1.06-μ region was monitored with another photomultiplier in order to assure the same excitation intensity. The minimum spectral slit width employed was about 0.5 Å. In the wavelength region longer than 1.1 μ, the specimen was excited with a 1-kW DXW Sylvania high-silica halogen lamp, and a Kodak PbS (type N-3) and a lock-in amplifier were employed for the detection. The spectral sensitivity of the detectors, in addition to the transmittance of the spectrometer, was calibrated by use of a quartz-iodine tungsten lamp whose spectral

[1] J. E. Geusic, E. O. Schulz-DuBois, and H. E. D. Scovil, Phys. Rev. **156**, 343 (1967).
[2] J. K. Neeland and V. Evtuhov, Phys. Rev. **156**, 244 (1967).
[3] J. E. Geusic (unpublished).
[4] The laser line wavelength at room temperature, 1.0648 μ, reported in the previous letter [J. E. Geusic, H. M. Marcos, and L. G. Van Uitert, Appl. Phys. Letters **4**, 182 (1964)], should be read as 1.0641 μ.

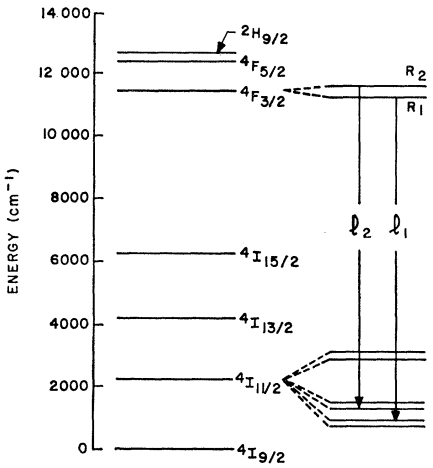

FIG. 1. Energy-level diagram of Nd^{3+} in YAlG. Emissions l_1 and l_2 correspond to the two transitions in the laser line (see Fig. 2).

radiant intensity had been measured and certificated at the National Bureau of Standards.

RESULTS AND ANALYSES

From the absorption coefficients determined for the slab, the peak absorption cross sections $\sigma_{R_1}=1.1\times10^{-20}$ cm^2 and $\sigma_{R_2}=4.1\times10^{-20}$ cm^2 were obtained for the R_1 (0.875 μ) and R_2 (0.869 μ) lines which correspond to the transitions from the ground state to the R_1 and R_2 levels of the $^4F_{3/2}$ state, respectively. Since all the degeneracy (except for Kramer's degeracy) of the relevant J manifolds is lifted in YAlG:Nd^{3+},[5] these absorption cross sections are equal to the emission cross sections for these lines. The peak cross section of the most intense absorption line ($^4I_{9/2}\rightarrow{}^4F_{5/2}$) at $\sim$8100 Å was 1.2×10^{-19} cm^2.

As seen in Fig. 2, the 1.064-μ laser line of YAlG:Nd^{3+} consists of two Lorentzian lines at room temperature. In order to compare our value with that of Neeland and Evtuhov, who did not take the overlapping into account, we shall define the effective emission cross section for the ion in the R_2 level of the $^4F_{3/2}$ manifold as follows:

$$\sigma_l=(\sigma_{l_1}/a)+\sigma_{l_2}, \tag{1}$$

where σ_{l_1} and σ_{l_2} are the cross sections of the two transitions at the laser line peak (1.0641 μ), and a is the Boltzmann factor between the R_1 and R_2 levels at room temperature ($\sim$0.66). With this effective cross section, the ratios of the peak emission intensities of the R_1 and R_2 lines to that of the laser line are given as

$$I_{R_1}/I_l=(\nu_{R_1}/\nu_l)^3\sigma_{R_1}/a\sigma_l,$$
$$I_{R_2}/I_l=(\nu_{R_2}/\nu_l)^3\sigma_{R_2}/\sigma_l, \tag{2}$$

where ν represents the transition frequency. By these relations, $\sigma_l/\sigma_{R_1}=83\pm7$ and $\sigma_l/\sigma_{R_2}=21\pm2$ were obtained from the measured ratios of the emission intensities. The latter value is compared to the ratio of 13.8 reported by Neeland and Evtuhov. In the determination of the ratio of the emission intensities, we took into consideration the self-absorption at the peak of the R_1 and R_2 lines and compared the result with that for a very thin slab (less than 0.8 mm in thickness). Using the values for σ_{R_1} and σ_{R_2} determined by the absorption measurement, we obtain the laser transition cross section $\sigma_l=8.7\times10^{-19}$ cm^2 ($\sigma_{l_1}=4.6\times10^{-20}$ cm^2, $\sigma_{l_2}=8.0\times10^{-19}$ cm^2). The values determined from the above two ratios agree with each other very well.

For a Lorentzian line, the transition probability A per ion in the initial level can be expressed as

$$A=(4\pi^2n^2\Delta_\nu/\lambda^2)\sigma^p, \tag{3}$$

where λ is the line wavelength, Δ_ν the full linewidth at half maximum, σ^p the peak cross section, and n the refractive index of the material. With measured values $\lambda_{l_1}=1.0645$ μ, $\lambda_{l_2}=1.0641$ μ, $\Delta_{\nu l_1}=4.2$ cm^{-1}, $\Delta_{\nu l_2}=5.2$ cm^{-1}, $\sigma_{l_1}{}^p=1.7\times10^{-19}$ cm^2, and $\sigma_{l_2}{}^p=8.0\times10^{-19}$ cm^2, we obtain $A_{l_1}=2.5\times10^2$ sec^{-1} and $A_{l_2}=14.4\times10^2$ sec^{-1} for the two transitions in the laser line. Again, if we define the effective radiative lifetime associated with the laser line as

$$\tau_l=[(A_{l_1}/a)+A_{l_2}]^{-1}, \tag{4}$$

we obtain $\tau_l=550$ μsec, in good agreement with previous measurements.[3,6] (The above effective radiative life-

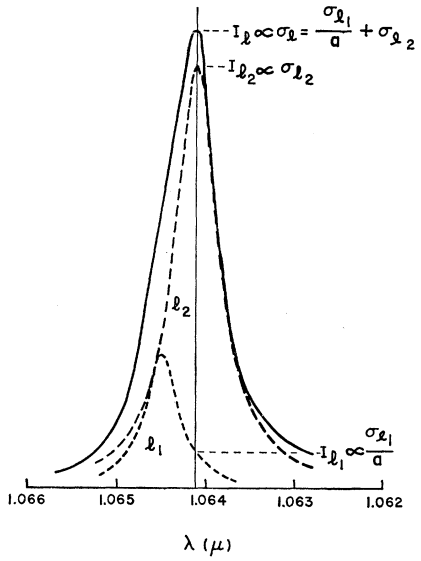

FIG. 2. Emission spectrum of 1.064-μ laser line at room temperature. Two Lorentzian lines contributing to the laser transition are shown by dashed curves.

[5] J. A. Koningstein and J. E. Geusic, Phys. Rev. **136**, A711 (1964).

[6] J. E. Geusic, H. M. Marcos, and L. G. Van Uitert, in *Physics Quantum Electronics*, edited by P. L. Kelly, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Company, Inc., New York, 1966), p. 725.

time, as well as the effective cross section, are defined only at room temperature, and readers are warned not to extrapolate the value to other temperatures.)

On the other hand, we can deduce the transition probability from the branching ratio and the fluorescence decay time. We define the branching ratio β of the transition $i \to f$ as follows:

$$\beta_{i\to f} = a_i A_{i\to f}/A_{\text{tot}}, \tag{5}$$

$$A_{\text{tot}} = a_1A_1 + a_2A_2 + a_3A_3 + \cdots,$$

where $a_i = \exp[-(E_i - E_1)/kT]$ is a Boltzmann factor, and $A_i = \sum_f A_{i\to f}$ is the total transition probability for all the radiative transitions initiating from state i. The initial states $i=1$ and 2 are the R_1 and R_2 levels, respectively, and $i=3$, 4, $\cdots$ represent the higher-lying states such as $^4F_{5/2}$, $^2H_{9/2}$, etc.

Since the relaxation times among the emitting states are very short, these levels are considered to be in thermal equilibrium. In fact, the thermalization between the two levels of the $^4F_{3/2}$ manifold has been established from the measurements of relative intensities of the fluorescence lines versus temperature,[7] and the fact that thermalization exists even in a YAlG:Nd^{3+} oscillator[6] indicates that the thermalization rate is very fast. On the contrary, the nonradiative multiphonon transitions from the emitting states to the lower ^4I states may be negligible, since the energy separation is several times greater than the phonon cutoff energy of the host crystal. In this case, the fluorescence decay time (the lifetime of the emitting states as a whole) τ can be written as

$$\tau = \sum a_i/A_{\text{tot}}. \tag{6}$$

Thus, for the two transitions in the laser line, we have

$$A_{l_1} = (\sum a_i/a_1)\beta_{l_1}/\tau,$$
$$A_{l_2} = (\sum a_i/a_2)\beta_{l_2}/\tau. \tag{7}$$

The branching ratio for each emission line in the 0.77- to 2.1-μ region was calculated from the emission spectrum. The branching ratios β_{l_1} and β_{l_2} were found to be 0.035 and 0.13, respectively. The estimated accuracy of the measurement is about $\pm 10\%$. Using the measured fluorescence decay time $\tau = 230$ μsec, we obtain $A_{l_1} = 2.6\times 10^2$ sec^{-1} and $A_{l_2} = 14.7\times 10^2$ sec^{-1}, which lead us to $\sigma_l = 8.9\times 10^{-19}$ cm^2. This value agrees well with the one determined by the other independent method. This agreement may justify our assumption that the contribution of nonradiative transitions to the fluorescence decay time is negligible compared with that of radiative processes.

[7] J. E. Geusic (unpublished).

The result of the measured branching ratio is summarized as follows:

$^4F_{3/2} \to {}^4I_{9/2}$	(0.87$\sim$0.95 μ)	0.25,
$^4F_{3/2} \to {}^4I_{11/2}$	(1.05$\sim$1.12 μ)	0.60,
$^4F_{3/2} \to {}^4I_{13/2}$	($\sim$1.34 μ)	0.15,
other ($^4F_{5/2} \to {}^4I_{9/2}$, etc.)		$\sim$0.01.

We did not observe the $^4F_{3/2} \to {}^4I_{15/2}$ emissions near 1.8 μ. The above result is very close to that for the transitions in Nd-doped barium crown glass measured by DeShazer and Komai[8]: 0.24 for 0.88-μ-group, 0.60 for 1.06-μ-group, and 0.16 for 1.35-μ-group emissions.[9] This is understandable, since the f-wave functions of rare-earth ions are hardly affected by the host material because of strong shielding.

Mauer[10] determined the laser transition cross section in Nd-doped glass by measuring 1.06-μ absorption at an elevated temperature. Though we also measured the absorption of YAlG:Nd^{3+} in the 1.06-μ region at 500°K, the absorption was too weak to determine the cross section accurately.

The value of $\sigma_l = 8.8\times 10^{-19}$ cm^2 is very large compared with emission cross sections $\sigma \sim 3\times 10^{-20}$ cm^2 of the R_1 line of ruby[11] and 1.06-μ line of Nd^{3+} in glass.[10] This fact, in addition to the four-level operation, negligible nonradiative decay rate, and good optical quality, clearly substantiates the excellence of YAlG:Nd^{3+} as a laser material. For optical refrigeration, the fact that the nonradiative decay rate is negligibly small is very important. The measured fluorescence branching ratio yields a value of 90 cm^{-1} ($\sim 4.3\times 10^{-22}$ cal) for the average phonon energy absorbed per one laser photon (1.0641 μ) absorbed in YAlG:Nd^{3+}. This result suggests that the temperature change because of optical refrigeration should be detectable in a thermally insulated YAlG:Nd^{3+} crystal when it is placed in a cavity of a currently available cw YAlG:Nd^{3+} laser. This experiment is now progressing in our laboratory.

ACKNOWLEDGMENTS

The authors are indebted to Miss D. M. Dodd for absorption measurements. Comments by J. P. Gordon are gratefully acknowledged.

[8] L. G. DeShazer and L. G. Komai, J. Opt. Soc. Am. **55**, 940 (1965).

[9] The definition of the ratio I_λ/I_{tot} in Table II of Ref. 8 is the same as that of our branching ratio [L. G. DeShazer and L. G. Komai (private communication)].

[10] P. Mauer, Appl. Opt. **3**, 433 (1964).

[11] D. M. Dodd, D. L. Wood, and R. L. Barns, J. Appl. Phys. **35**, 1183 (1964).