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LIFETIME OF THE EXCITED STATE $^4F_{3/2}$ *OF THE* Nd^{3+} *ION IN* CaF_2 *AND* $CaWO_4$

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The lifetime of the excited state $^4F_{3/2}$ of the Nd^{3+} ion in CaF_2 and $CaWO_4$ was investigated over a wide range of temperatures at Nd^{3+} concentrations ranging from several thousandths of a per cent to several per cent. The influence of nonradiative transitions was analyzed. A simple design of a taumeter is described.

INTRODUCTION

ONE of the principal characteristics of excited states is their lifetime, which is directly associated with the probability of spontaneous emission of radiation. The case of low probability of spontaneous emission from a given excited level, when the system is in a metastable state, is of special interest. Such systems can be important because they make it possible to accumulate energy.

Apart from their spontaneous emission of radiation, excited systems may dissipate energy by nonradiative transitions. If the nonradiative transition probability is high compared with the probability of spontaneous transitions, the lifetime of the excited state is reduced in accordance with the relationship

$$1/\tau_\Sigma = 1/\tau_{sp} + 1/\tau_{nonr}, \qquad (1)$$

where τ_Σ is the total lifetime of the excited state, τ_{sp} is the spontaneous transition lifetime, and τ_{nonr} is the lifetime of the nonradiative transition.

The probability of spontaneous radiation from a rare-earth ion is governed mainly by the interaction of its states, which depends also on the surrounding medium. The probability of nonradiative transitions is associated with the lattice vibrations.

We investigated the lifetimes of the excited level $^4F_{3/2}$ of the Nd^{3+} ion in CaF_2 and $CaWO_4$ crystals in the temperature range from 300 to 4.2°K at Nd^{3+} concentrations ranging from thousandths of a per cent to several per cent. Since these crystals are used in lasers working at room temperature,[1,2] we analyzed the influence of the nonradiative transitions on the reduction of the lifetime of the excited state $^4F_{3/2}$. A description is given of a simple taumeter, by means of which the aforementioned investigations can be carried out.

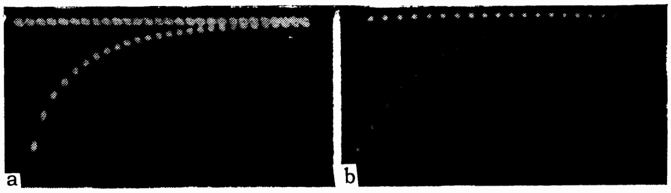

FIG. 1. Decay of the luminescence of Nd^{3+} in CaF_2 at 300°K (a) and at 77 and 4.2°K (b). Time marks are given every 200 μsec.

EXPERIMENTAL RESULTS AND DISCUSSIONS

We used $CaF_2:Nd^{3+}$ crystals grown from the melt in a fluorinating atmosphere by lowering a crucible containing from 0.003 to 2.0 wt.% of NdF_3. The samples were excited with light pulses of ≈ 10–15 μsec duration and about 5 J energy, with wavelengths lying in the intense absorption bands in the range 0.5–0.9 μ. The luminescence was recorded, after passing through a ZMR-3 monochromator with a photomultiplier having an oxygen–cesium photocathode. The photomultiplier signal was fed to an oscillograph of the ÉNO-1 type.

Figure 1 shows photographs of the oscillograms of the luminescence decay of a CaF_2 crystal with about 0.4% Nd^{3+}, at three temperatures. It is evident that the luminescence decay curve consists of two parts, which are characterized by two time constants - long and short. These curves can be satisfactorily represented by two exponential functions. The presence of two exponentials should be ascribed to the fact that some Nd^{3+} ions are in a crystal electric field of tetragonal symmetry while others are in a field of orthorhombic symmetry.[3] At an Nd^{3+} concentration of about 0.4%, the spectra corresponding to these two symmetries

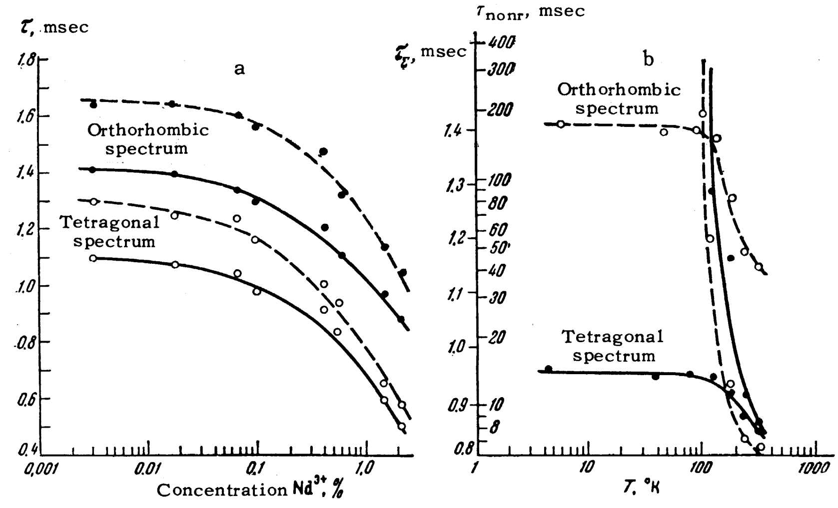

FIG. 2. Lifetime of the excited state $^4F_{3/2}$ of the Nd^{3+} ion in CaF_2: a) as a function of the active center concentration (the continuous curves represent 300°K and the dashed curves 77 and 4.2°K); b) as a function of temperature at a Nd^{3+} concentration of about 0.4%.

are of approximately equal intensity. From an analysis of the forms of the exponential curves at low temperatures and from the results obtained by the utilization of the optical absorption spectra, luminescence, and e.s.r. spectra, we may conclude that in crystals with different concentrations of Nd^{3+} the long time constant corresponds to the orthorhombic spectrum, and the short time constant, to the tetragonal spectrum.

Figure 2 shows the dependence of the decay time of Nd^{3+} in CaF_2 on temperature and on the active ion concentration. It is evident from Fig. 2a that the luminescence lifetime of the $^4F_{3/2}$ level becomes longer as the change is made from room temperature to nitrogen temperature and below. This may be explained as follows. At 300°K, the nonradiative transition probabilities are comparable with the spontaneous transition probabilities, and we observe the net lifetime; at low temperatures, the nonradiative transition probability decreases and we observe the time which represents purely spontaneous transitions. Using this interpretation, we can employ Eq. (1) to determine simply the lifetime for nonradiative transitions from the $^4F_{3/2}$ level. The results of such calculations are shown in Fig. 2b. It is evident that at approximately 100°K and at lower temperatures the excited-state lifetime is determined by the spontaneous lifetime, but at higher temperatures the nonradiative transitions begin to have an effect and the net lifetime starts to decrease.

Crystals of $CaWO_4$ containing Nd^{3+} were grown by the Czochralski method, using from 0.05 to 6% Nd_2O_3. The excess Nd^{3+} electric charge was compensated by the alkali metal Na^+, which was introduced in amounts which represented different proportions by weight with respect to Nd_2O_3. In the majority of the crystals, the ratio of Nd_2O_3 to Na by weight was 1 : 5. In the investigation of the luminescence decay of Nd^{3+} in $CaWO_4$, the duration of the exciting light pulse was ≈ 5–8 μsec and the pulse energy was ≈ 1 J. The method and apparatus used to record the luminescence decay were the same as before.

Figure 3 shows an oscillograph of the luminescence decay of the $^4F_{3/2}$ level for a sample containing about 1% Nd^{3+}. The investigations of the temperature dependence of the luminescence decay from 300 to 4.2°K showed that the lifetime of the $^4F_{3/2}$ level remained constant and obeyed rigorously the exponential law. This is in good agreement with the data obtained in the investigation of the e.s.r. spectrum of Nd^{3+} in $CaWO_4$. They show that Nd^{3+} has only one type of spectrum which is due to a crystal electric field of tetragonal symmetry.[4] The lack of dependence of the luminescence decay time on temperature follows from the fact that the probabilities of nonradiative transitions from the $^4F_{3/2}$ level in the $CaWO_4$ lattice are low and the nonradiative transition times are considerably longer than the spontaneous radiation times.

Figure 4 shows the dependence of the lifetime of the $^4F_{3/2}$ level on the concentration of Nd^{3+}. At low Nd^{3+} concentrations, up to 0.5-0.6%, the lifetime remains practically constant and begins to decrease only on further increase of the concentration. The reason for this decrease of the lifetime, which occurs also in the case of CaF_2, is not yet

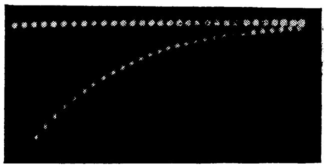

FIG. 3. Decay of the luminescence of Nd^{3+} in $CaWO_4$. Time marks are given every 20 μsec.

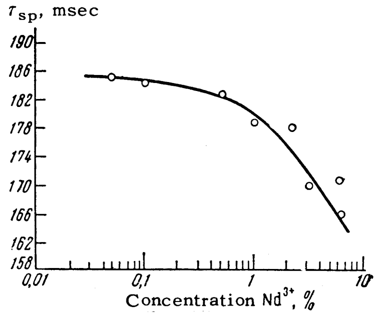

FIG. 4. Lifetime of the excited state $^4F_{3/2}$ of the Nd^{3+} ion in $CaWO_4$ as a function of the Nd^{3+} concentration.

quite clear. It may possibly be associated with the distortion of the symmetry of the Nd^{3+} ion environment at high neodymium concentrations. On the other hand, it may be explained also by the magnetic dipole-dipole interaction of Nd^{3+} ions.

EXPERIMENTAL APPARATUS

To investigate the luminescence decay time within the range from 30 μsec to tens of milliseconds, from 3600 to 11 000 Å, and over a wide range of temperatures (from room temperature to 4.2°K), we developed a taumeter whose block diagram is given in Fig. 5.

A stroboscopic lamp of the ISSh-100-3 type (1), placed at one of the foci of an elliptic mirror (2) of 250 mm diameter, was used as the source of light pulses. The electrical power supply for the lamp was a capacitor bank (3) which could deliver from 0.5 to 50 J. The lamp was triggered using a circuit similar to that described in the technical certificate of the lamp. At minimum capacitances of the supply bank (0.1 and 0.25 μF), the light pulse was of about 5–7 μsec duration. The pulse which triggered the lamp also synchronized the beginning of the sweep of the ÉNO-1 oscillograph (4).

The crystal under investigation was placed at the second focus of the mirror, in a tubular glass cryostat having a plane parallel exit window (6). The luminescence from the crystal passed through the exit window of the cryostat to the entrance aperture of a type ZMR-3 monochromator (7). One end of the tubular cryostat was connected by a tube to a standard cryostat, which contained a liquefied gas (8 or 9). The same cryostat had an electric heater in the form of the usual wire or carbon resistor (10). The gas formed on heating passed through the tubular cryostat and cooled it. Using argon, we were able to obtain temperatures down to 80°K, while with helium the minimum temperature was 15°K. The required temperature could be established smoothly by varying the vapor velocity in the tubular cryostat by changing the rate of heating, using an autotransformer (11). The temperature of the crystal was recorded with a copper-constantan thermocouple (12) with respect to the liquefied gas. A dc millivoltmeter V2-3, served as an indicator (13). The thermal contact between the thermocouple and the crystal was ensured by a tight teflon coupling (14).

To absorb the light not needed in the excitation of the luminescence, we used light filters of colored glass (15). A photomultiplier (5) was

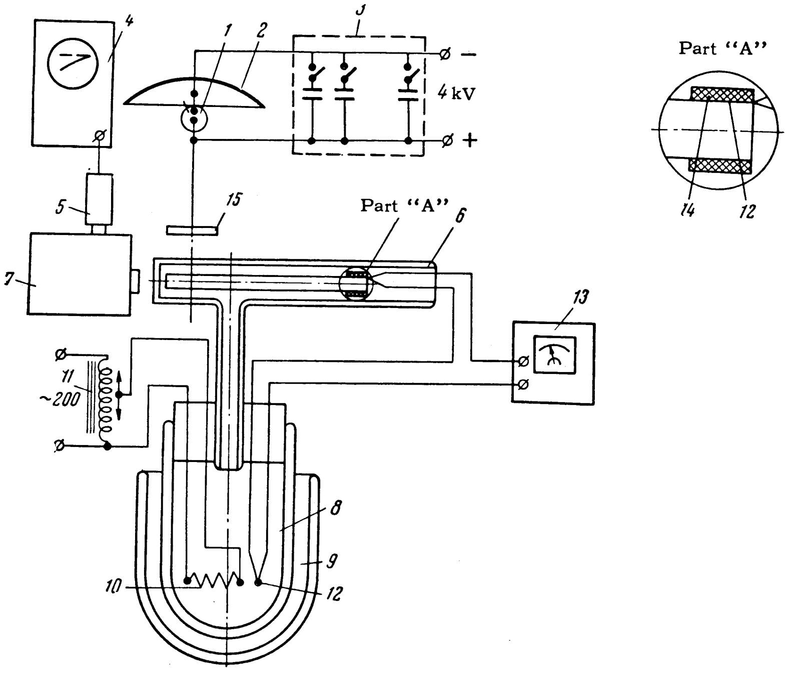

FIG. 5. Block diagram of the pulse taumeter.

placed at the exit of the ZMR-3 and the photomultiplier signal was applied to the terminals of the vertical amplifier of the oscillograph. The beam scan was calibrated with time marks.

Using this apparatus, we were able to change over crystals rapidly and to reach the required temperature fast. In recording the luminescence decay at 4.2°K, we employed a standard cryostat and the crystal under investigation was placed directly in liquid helium. The accuracy of the measurement of the luminescence decay time of Nd^{3+} in CaF_2 was ±20 μsec, while in the case of Nd^{3+} in $CaWO_4$ it was ±2 μsec.

CONCLUSIONS

The results of this investigation of the luminescence decay time of CaF_2 and $CaWO_4$ containing Nd^{3+} as a function of temperature and Nd^{3+} concentration lead to the following conclusions.

1. As the Nd^{3+} concentration in CaF_2 is increased, the lifetime of the excited state $^4F_{3/2}$ decreases in both types of spectra (the tetragonal and orthorhombic), and this decrease is particularly strong at Nd^{3+} concentrations higher than 0.7%. In $CaWO_4$ crystals, this strong decrease occurs at higher concentrations.

2. In CaF_2 at room temperature, the nonradiative transitions, which reduce considerably the spontaneous transition lifetime, play the dominant role. At nitrogen and lower temperatures in the case of CaF_2 and at all temperatures in the case of $CaWO_4$, the lifetime of the excited state $^4F_{3/2}$ is governed only by the spontaneous radiation.

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