INVESTIGATION OF THE LUMINESCENCE LINE WIDTH AND TEMPERATURE SHIFT OF THE FREQUENCY OF A CW $CaF_2:Dy^{++}$ *LASER*

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It is shown that broadening of the luminescence line ($7T_1^{(2)} \rightarrow 8T_2^{(2)}$ transition) is homogeneous and is due to the lifetime of the ground level of $8T_2^{(2)}$. An explanation is given for the frequency shift due to temperature of a CW $CaF_2:Dy^{++}$ laser.

CRYSTALS of CaF_2 activated by divalent dysprosium are important for the realization of pulsed and CW lasers at 2.36 nm.[1-3]

Kiss[4] has carried out a detailed spectroscopic investigation of Dy^{++} in the cubic lattice of CaF_2 and also obtained the temperature dependence of the width and shift of the luminescence line ($\lambda = 2.36$ nm). However, he does not give a theoretical explanation of the reason for the broadening of the luminescence line and its shift, which is extremely important for the elucidation of the dynamic processes in the laser.

In this paper we calculate the probabilities of nonradiative transitions of the Dy^{++} ion in CaF_2, which cause homogeneous broadening of the luminescence line, and also investigate the temperature dependence of the frequency shift of the CW $CaF_2:Dy^{++}$ laser in the vicinity of 78° K.

The Dy^{++} ion in CaF_2 is situated in a crystalline field of cubic symmetry created by the F^- ions. The separation between the term $^5I_8$ and the first excited term $^5I_7$ is 4126 cm^{-1} and is due to spin-orbit interaction. In a cubic field there is a further splitting of these terms (Fig. 1), and laser action occurs in the luminescent transition $7T_1^{(2)} \rightarrow 8T_2^{(2)}$ at a wavelength of 2.36 nm. The width of this luminescence line is composed of the widths of the initial $7T_1^{(2)}$ and the final $8T_2^{(2)}$ levels. The width of the metastable level $7T_1^{(2)}$ is determined by its lifetime $\tau \approx 12 \times 10^{-3}$ sec,[4] and the width of the level $8T_2^{(2)}$ is determined by the probabilities of nonradiative transitions from the latter.

As will be seen from the calculations presented below, the probabilities of nonradiative transitions from the level $8T_2^{(2)}$ in the temperature interval 4.2 to 80° K are of the order of 10^{10} sec^{-1}, and so the width of the luminescence line is mainly determined by the width of the level $8T_2^{(2)}$. As follows

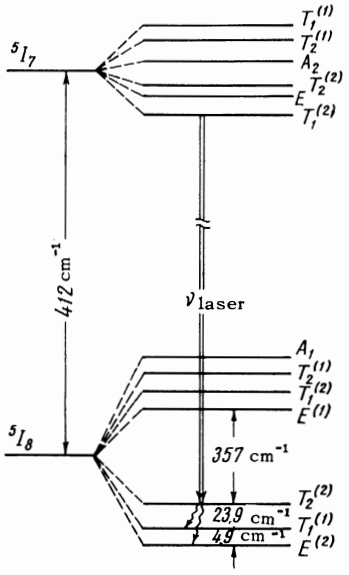

FIG. 1. Splitting of the energy levels of the Dy^{++} ion in the cubic field of the CaF_2 crystal.

from the experimental data of Kiss,[4] inhomogeneous broadening of the luminescence line on account of defects in the $CaF_2:Dy^{++}$ crystals is insignificant. The transition of the ion to the ground state $8E^{(2)}$ occurs in a nonradiative manner on account of the electron-vibrational interaction, and the energy of the ion is transferred to the lattice vibrations of CaF_2.

We calculated the probabilities of the nonradiative transitions $8T_2^{(2)} \rightarrow 8E^{(2)}$, $8T_2^{(2)} \rightarrow 8T_1^{(1)}$ in the harmonic approximation, using perturbation theory. In the nonradiative transition $T_2^{(2)} \rightarrow E^{(2)}$ the lattice vibrations have to take up an energy of 28.8 cm^{-1} and in the transition $T_2^{(2)} \rightarrow T_1^{(1)}$, an energy of 23.9 cm^{-1}; there are corresponding oscillators in the Debye spectrum of the lattice vibrations of CaF_2 ($\Theta = 320$ cm^{-1}). In this case a single-phonon nonradiative transition is possible. Hence

it is sufficient to carry out the calculation by first-order perturbation theory.

The formula for calculating the probability of a single-phonon nonradiative transition has the form

$$W(\Gamma \to \Gamma') = \frac{2\pi}{\hbar^2 g(\Gamma)} \sum_{\alpha=1}^{g(\Gamma)} \sum_{\beta=1}^{g(\Gamma')} \langle | (\hat{\mathcal{H}}_{e\text{-}v})_{\Gamma_\alpha n_j, \Gamma_\beta' n_i'} |^2 \rangle_{Av} \rho(\omega),$$

where $g(\Gamma)$ is the degree of degeneracy of the level Γ, $\rho(\omega) = V\omega^2/\pi^2 v_t^3$ is the Debye density of the frequency distribution in the transverse crystal vibrations, v_t is the speed of propagation of transverse vibrations in the crystal, V is the volume of the crystal. The sign $\langle\ \rangle_{Av}$ indicates an average over all directions of propagation and polarization of the lattice vibrations and over the occupation numbers of the lattice oscillators, $\hat{\mathcal{H}}_{e-v}$ is the electron-vibrational interaction operator.[5]

In the calculation of the probabilities of the nonradiative transitions we have used the following data:

1) The wave functions and crystal field parameters for $CaF_2:Dy^{++}$ were taken from [4];

2) $\bar{r}^2 = 0.2534$ Å^2, $\bar{r}^4 = 0.1716$ Å^4, $\bar{r}^6 = 0.2443$ Å^6 —according to [6];

3) the density $d = M/V = 3.2$ g/cm^3;

4) the speed of propagation of the transverse vibrations in the CaF_2 crystal $v_t = 3.8 \times 10^5$ cm/sec.

At the temperature $T = 0°$ K the probabilities of the nonradiative transitions $8T_2^{(2)} \to 8E^{(2)}$, $8T_2^{(2)} \to 8T_1^{(1)}$ are respectively $W_1 = 6.61 \times 10^9$ sec^{-1}, $W_2 = 7.13 \times 10^9$ sec^{-1}, and the total broadening of the luminescence line amounts to 0.073 cm^{-1}.

The temperature dependence of the probability of single-phonon nonradiative transitions is determined by the relation

$$W_T = W_0(\Gamma \to \Gamma') e^{\Delta(\Gamma\Gamma')/kT} / e^{\Delta(\Gamma\Gamma')/kT} - 1.$$

The table shows the values of the calculated probabilities of nonradiative transitions for various temperatures, as well as the calculated and experimental values of the luminescence line width. A comparison of the calculated and experimental data for the line width of the luminescence line shows that at low temperatures $T \lesssim 78°$ K, the broadening of the line occurs on account of the single-phonon nonradiative transitions $8T_2^{(2)} \to 8E^{(2)}$, $8T_2^{(2)} \to 8T_1^{(1)}$.

At temperatures above 78° K, the luminescence line broadening has to be explained by taking into account multi-phonon nonradiative transitions from the level $8T_2^{(2)}$ via the virtual levels $E^{(1)}$, $T_1^{(2)}$, $T_2^{(1)}$, and A_1. In a paper by Galaktionova et al.[7] the luminescence line width is attributed to inhomogeneous broadening. By comparing their data with the work of Kiss[4] one may assume that the $CaF_2:Dy^{++}$ crystal that they investigated has a relatively large number of lattice defects, which indeed bring about inhomogeneous broadening of the luminescence line.

Our investigation of the dependence of the frequency shift of the CW $CaF_2:Dy^{++}$ laser was carried out in the vicinity of 78° K. The concentration of Dy^{++} was 0.03%. The resonator consisted of dielectric mirrors applied to the end surfaces of the crystal having reflection coefficients of 84 and 100%. The crystal was placed in a quartz dewar and cooled by supercooled liquid nitrogen, which was forced through the dewar under pressure. The pumping lamp and dewar were located in an elliptical illuminator.

The temperature of the crystal was varied by changing the temperature of the supercooled nitrogen. The temperature of the nitrogen coming out of the dewar was measured with a thermocouple calibrated in the range 68 to 78° K.

A Fabry-Perot interferometer with a mirror spacing t = 3 cm served as the spectral instrument. The pressure of the air within the interferometer was varied; this produced a scanning of the intensity of the zero-order Fabry-Perot interference ring. The laser radiation was recorded with the apparatus described in [8].

In one measurement cycle the positions of the maxima of zero order with respect to pressure in the interferometer were determined at different temperatures of the supercooled nitrogen, with constant pumping and a constant rate of flow of the nitrogen. The temperature shift of the frequency was determined from the formula

$$\Delta\nu = \Delta p / 2tD\Delta T \quad [\text{cm}^{-1}/\text{deg}]$$

where Δp is the shift of the zero-order maximum (in units of pressure) due to the change in temperature of the crystal; t is the length of the Fabry-

T, °K	$W_1\left(8T_2^{(2)} \to 8E^{(2)}\right)$, 10^9 sec^{-1}	$W_2\left(8T_2^{(2)} \to 8T_1^{(1)}\right)$, 10^9 sec^{-1}	$W = W_1 + W_2$, 10^9 sec^{-1}	$\Delta\nu_{calc}$, cm^{-1}	$\Delta\nu_{exp}$ [4], cm^{-1}
0	6.61	7.13	13.74	0.073	—
4,2	6.61	7.13	13.74	0.073	<0.07
27	8.43	9.92	18.35	0.097	~ 0.10
78	16.06	20.04	36.10	0.192	0.25
193	34.88	43.35	78.23	0.415	2.5

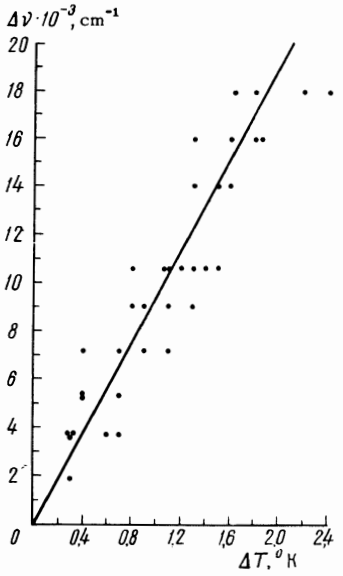

FIG. 2. Dependence of the frequency shift of the $CaF_2:Dy^{++}$ laser on crystal temperature. (The arrangement of the points in horizontal and vertical lines is due to the discrete markings of the measuring instruments).

Perot interferometer; D is the spacing between adjacent maxima of the interference pattern (in pressure units); ΔT is the temperature change of the crystal.

We carried out experiments on several crystals with different pumping and found that when the temperature of the crystal was changed by 1°, the laser frequency changed by 0.0095 ± 0.0025 cm^{-1}. Figure 2 gives the dependence of the frequency shift of the laser on the temperature change of the crystal. The scatter of the experimental points is due to the large relative error of a single measurement (about 40 to 50%). When the crystal is cooled the zero-order maximum (in pressure units) shifts toward higher pressures. This indicates that when the crystal is cooled the laser frequency shifts toward shorter wavelengths.

On the other hand, by using the data of Kiss,[4] one can empirically derive the dependence of the luminescence line frequency on the crystal temperature (T = 0 to 193° K), which has the form (T in ° K)

$$\nu(T) = \nu_0 - 4.95 \cdot 10^{-5} T^2 - 5.06 \cdot 10^{-9} T^3,$$

and for a change in crystal temperature of 1° the frequency shift of the luminescence line equals $\Delta\nu \approx 0.0077$ cm^{-1}/deg.

If the measurement errors are taken into account, our measurements of the frequency shift of the CW laser agree with the experimental data on the shift of the luminescence line presented in [4,7].

The temperature shift of the laser frequency can be explained in the following way: when the crystal temperature changes, the lattice constant changes and with it the crystalline field. The change in crystalline field leads to a shift of the energy levels of the Dy^{++} ion (Fig. 1), and as a consequence the spacing between the levels $7T_1^{(2)}$ and $8T_2^{(2)}$ changes, which leads to a change in the laser frequency. The crystal field potential for Dy^{++} in CaF_2 contains terms of the fourth and sixth degree, in which R (the distance between the Dy^{++} ion and the nearest F^- ion) enters respectively as R^{-5} and R^{-7}.

In making an estimate of the laser frequency shift due to a change in the crystal field with temperature, we made use of the coefficient of linear expansion for the CaF_2 lattice given by Batchelder and Simmons.[3] The calculated value of the frequency shift for a change in temperature of 1° in the vicinity of 78° K equals $\Delta\nu = 0.0041$ cm^{-1}. This is approximately one-half the experimental value obtained by us and in [4,7]. It may be that this discrepancy is due to the fact that for $CaF_2:Dy^{++}$ the point-charge model for the crystal field is not a good approximation for explaining the observed phenomena.

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