

RARE-EARTH CHELATE LASERS

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RUBY lasers and neon-helium gas lasers were the first sources of stimulated radiation in the optical region of the spectrum. The remarkable properties of laser emission—its coherence, monochromaticity, and high directional definition resulting in great power—have engendered enormous interest in the systems that can be used to realize laser action. All these extremely diversified systems permit the inversion of energy level populations. As a result, stimulated emission can exceed absorption; in other words, light is amplified.

The basic problem that must be solved in designing any laser is the selection of a system with sufficiently high energy gain. This gain depends on the pumping energy, and also on the parameters of the (active) amplifying medium—the emission line width, quantum yield of luminescence for this line, spectral width, and absolute amount of absorption. Immediately after the first lasers were constructed an active search was begun for compounds whose spectral properties lead to high gain. It was necessary to expand the class of lasing substances because practical applications require lasers for different spectral regions and possessing different emission properties, and also because the investigation of physical processes in the lasers themselves necessitates the availability of systems based on different principles. The exploratory investigations turned increasingly to the study of inorganic crystals and glass that can be activated by small amounts of rare-earth elements, whose luminescence is characterized by extremely intense narrow lines. Such crystals as fluorites and tungstates doped with samarium, dysprosium, and neodymium, and also neodymium-doped glass have been used widely in different lasers.

In addition, Rautian and Sobel'man suggested, as early as 1961, that organic complexes with rare-earth elements (chelates) could be used in lasers.^[1] The same idea was developed in ^[2,3]. The broad absorption bands of rare-earth chelate are associated with the organic part of the molecules, while the narrow emission lines characterize the metal in the compound. The great diversity of chelates with different combinations of rare-earth ions and organic molecules could considerably expand the emission frequency range. In the last two years interest in rare-earth chelates has been considerably intensified. This is evident from the numerous publications concerned with their synthesis and spectral properties, as well as with their utilization to produce laser action. We here present

a brief description of the properties and peculiarities of oscillation in solutions of rare-earth chelates.

1. SPECTRAL PROPERTIES OF RARE-EARTH CHELATES

Chelates are complex groups in which organic molecules (ligands) are attached to an ion (here a rare earth metal) by so-called "clawlike" (chelate) bonds. The number of ligands attached to the ion depends on the coordination nonsaturation of the compound and the number of unoccupied orbitals of the rare-earth ion, steric factors, and the electron-donor properties of the ligands. In the numerous class of chelates used for laser oscillation the most interesting are the complexes of rare-earth ions and β diketones. A typical example is Eu-benzoylacetone, whose structural formula is shown in Fig. 1. We here have a three-ligand complex. Four-ligand rare-earth complexes of β -diketones are also known. In this case the electrical neutrality of the molecule is conserved by charge-compensating additives such as piperidine, morpholine etc.

The substances used in lasers should possess the following spectral properties: 1) A small number of narrow ($\sim \text{cm}^{-1}$) fluorescence lines; b) a quite high fluorescence quantum yield from the required transitions; c) strong absorption bands. We shall now consider to what extent the rare-earth chelates satisfy these requirements.

The specific spectral properties of chelates are determined by the transfer of energy from the organic part of the molecule to the rare-earth ion. This energy transfer proceeds as follows (Fig. 2). Energy absorbed by the organic part of the molecule raises the latter to an excited singlet state (2). After a very short time ($\tau < 10^{-8}$ sec) the molecule undergoes a

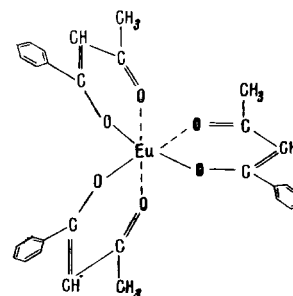


FIG. 1. Structure of a molecule of Eu-benzoylacetone.

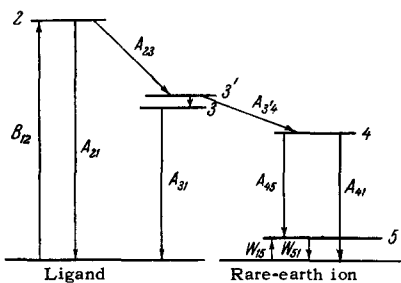


FIG. 2. Energy-level scheme of rare-earth chelates. 1 – Ground state, 2 – excited singlet state of ligand, 3 and 3' – excited triplet states of ligand, 4 – excited state of rare-earth ion, 5 – vibrational state of rare-earth ion.

transition to a triplet state (3). If the triplet state of the ligand lies higher than the upper excited rare-earth ion state (4), the ion can receive energy and emit radiation that is characteristic of the rare earth. In some cases this energy transfer is highly efficient and ensures a high quantum yield of chelate luminescence. No ligand phosphorescence is observed. When the energy-transfer efficiency is not high two competing processes occur—emission from the ligand triplet state and energy transfer to the rare-earth ion. It is interesting that in this case the decay time of rare-earth luminescence is shorter than that of ligand luminescence. This latter circumstance shows that energy is transferred from either the vibrational triplet level or from a higher-lying triplet state (3'). If the rare-earth level is energetically unsuitable for this transfer we observe only ligand luminescence. With respect to stimulated emission the first case is most interesting; here we have narrow emission lines that are characteristic of the rare-earth ion, and which we shall now discuss. As an example we shall consider the luminescence of Eu-benzoylacetonate [Eu(BA)], which is used most widely in liquid lasers.

The luminescence spectrum of Eu(BA) solutions consists of an isolated line at 5790 Å, several lines in the vicinity of 5370 Å, 5900 Å, and 6500 Å, and also intense emission in the region 6100–6200 Å (Fig. 3). The observed spectrum of the solution differs somewhat from the luminescence spectrum of the free Eu^{3+} ion

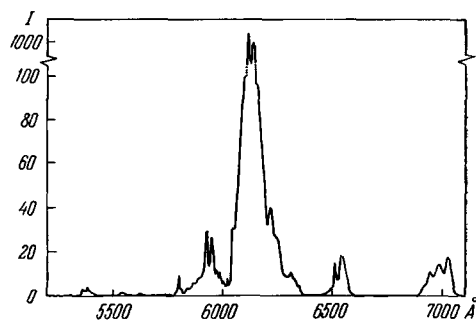


FIG. 3. Luminescence spectrum of Eu-benzoylacetonate in an alcohol solution.^[4]

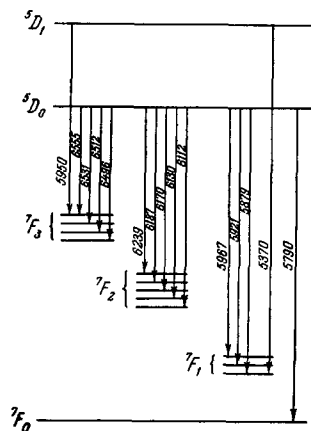


FIG. 4. Energy level scheme of Eu^{3+} in Eu-benzoylacetonate.

because of the influence of the ligand field and of the solvent field. Therefore, although the Eu^{3+} spectrum has undergone frequent detailed investigation,^[5,6] the identification of the chelate lines from the level scheme was of independent interest. The isolated 5790-Å line observed in both luminescence and absorption was identified^[4] as representing a ${}^5\text{D}_0$ - ${}^7\text{F}_0$ transition, for which splitting should not be observed since $J = 0$ (Fig. 4). The remaining groups of lines were assigned on the basis of a comparison between the decay times of luminescence in the different spectral regions, coming from Eu(BA) crystals at a low temperature.^[7] The lines in the 5790, 5950, and 6120 Å regions have the identical lifetime $\sim 550 \pm 50 \mu\text{sec}$, and were therefore assigned to transitions from a single ${}^5\text{D}_0$ level. The 5370-Å line with a lifetime below $10 \mu\text{sec}$ was assigned to a transition from a higher level (${}^5\text{D}_1$). A detailed analysis of the luminescence spectrum showed that the ${}^7\text{F}_1$ level undergoes triple splitting, while the ${}^7\text{F}_2$ level is split into five sublevels. The strongest fluorescence lines represent a transition from ${}^5\text{D}_0$ to ${}^7\text{F}_2$, which is 1000 cm above the ground level; 75% of the emitted energy is concentrated in these lines.

The intensities and shapes of the lines included in the aforesaid transition are very sensitive to the characteristics of chelate structure.^[8] Four-ligand compounds are characterized by a larger number of highly intense narrow lines. For 3-ligand chelates the given spectral region exhibits a small number of broader, overlapping, lines with considerably lower intensities. This is well demonstrated by the luminescence spectra of $\text{Eu}(\text{BA})_3$ and $\text{Eu}(\text{BA})_4$ in alcohol solutions (Fig. 5). The narrower lines and higher emission intensities make the 4-ligand chelates more promising for use in lasers.

Luminescence properties are also affected by different impurities (piperidine, morpholine etc.) that accompany the ligands. Variation of the amounts of these impurities will slightly shift the principal lines of the ${}^5\text{D}_0$ - ${}^7\text{F}_2$ transition and alter their shapes and intensities. For example, in the case of $\text{Eu}(\text{BA})_4$ -piperi-

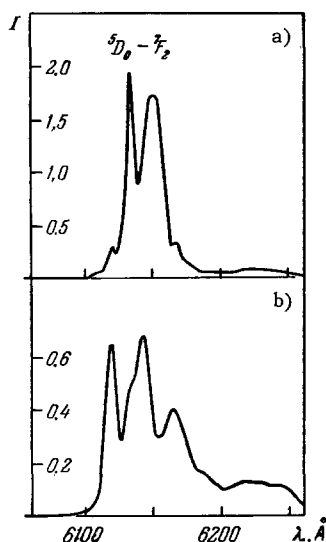


FIG. 5. Group of strongest lines emitted by alcohol solutions of (a) $\text{Eu}(\text{BA})_4$, and (b) $\text{Eu}(\text{BA})_3$.

dine crystals these lines lie at 6125 and 6133 Å, while for $\text{Eu}(\text{BA})_4$ -diethylamine they lie at 6117 and 6140.8 Å;^[9] for $\text{Eu}(\text{BA})$ -Na there is one line at 6111 Å.^[10] There is the additional possibility that we might synthesize compounds which would have the most suitable laser properties.

The emission energy distribution among the lines of the ${}^5\text{D}_0$ - ${}^7\text{F}_2$ transition depends strongly on temperature.^[4] Figure 6 shows the temperature dependence of the strongest lines from an alcohol solution of $\text{Eu}(\text{BA})_4$. With decreasing temperature we observe a redistribution of energy that favors the 6130-Å line and reduces its width to 21 cm^{-1} . At the same time we observe an overall rise of intensity as the luminescence quantum yield grows. The quantum yield in the 6130-Å line increases to 10% at -150°C .^[11] This increase results from both the "freezing" of nonradiative processes and the enhanced efficiency of energy transfer to the ion. Estimates given in^[4] indicate that at nitrogen temperature the energy-transfer efficiency is five times greater than at room temperature.

The quantum yield also depends strongly on the solvent. Thus for Eu-tenoyltrifluoroacetate (EuTTA) the

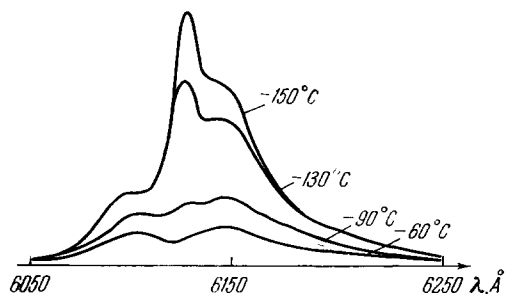


FIG. 6. Group of strongest lines emitted by alcohol solution of $\text{Eu}(\text{BA})_4$ at different temperatures.

quantum yield varies from 0.19 in an alcohol solution to 0.56 in an acetone solution at room temperature.^[12] The variations of the quantum yields of different chelates as functions of the solvent and temperature have been studied thoroughly in^[12-15]. By lowering the temperature and selecting a suitable solvent we can achieve the optimal conditions for a high luminescence quantum yield.

The absorption spectra of rare-earth chelate solutions comprise a broad band in the 2000-4000-Å region, often with two peaks belonging to the ligand. Since the ligands are complex organic molecules having a system of conjugate bonds, this absorption is very intense. If the ligand is benzoylacetone the absorption coefficient of the chelate is $\sim 10^5\text{ cm}^{-1}\text{-mole}^{-1}$ at the maximum. When the rare-earth ion is changed the absorption is not affected appreciably.^[13-15] The absorption attributable to the rare-earth ion is extremely small, and its observation in the 5000-7000 Å region encounters certain experimental difficulties (the great length of the experimental vessel, temperature stabilization etc.). For $\text{Eu}(\text{BA})$ the measured value of this absorption was $0.1\text{ cm}^{-1}\text{-mole}^{-1}$.^[4]

The narrow lines and high quantum yield, together with the broad absorption bands of the rare-earth compounds with β -diketones, make these substances good prospects for utilization in lasers.

2. SOME PROPERTIES OF CHELATES AS LASER MATERIALS

The level scheme of rare-earth chelates in Fig. 2 essentially repeats the familiar four-level scheme describing the oscillation cycle for several solids (the fluorites of uranium and samarium, neodymium wolframite etc.) The most important feature of the scheme is the fact that the stimulated emission from level 4 goes to a lower level 5 that is not the ground level. If level 5 lies high above the ground level its population will be insignificant even at room temperature. Therefore the inversion required for oscillation requires that state 4 receive considerably fewer molecules than in the case of a three-level system, where this number must comprise more than half of the total number of molecules.

Many rare-earth chelates exhibit radiative transitions for which level 5 is a few hundred cm^{-1} above the ground state. At a sufficiently high pumping rate we obtain oscillation at the frequency corresponding to the transition from level 4 to level 5. For chelates with Eu this transition is ${}^5\text{D}_0$ - ${}^7\text{F}_2$.

A probability calculation can be used to determine which parameters govern the population of level 4 in Fig. 2. We use the following notation: B_{12} is the probability of molecular excitation to the singlet state, depending on the absorption cross section and intensity of excitation radiation; A_{21} and A_{31} are the probabilities of ligand fluorescence and phosphorescence; A_{45}

is the probability that the rare-earth ion will spontaneously emit the laser line; A_{41} is the probability of two other processes that deplete level 4; W_{15} and W_{51} are the probability of a transition from the ground state to a vibrational state and vice versa; $A_{23'}$, $A_{3'3}$, and $A_{3'4}$ are the probabilities of nonradiative transitions. The molecular concentration N in the different excited states varies with time as follows:

$$\begin{aligned}\frac{dN_2}{dt} &= B_{12}N_1 - (A_{21} + A_{23'})N_2, \\ \frac{dN_{3'}}{dt} &= A_{23'}N_2 - (A_{3'3} + A_{3'4})N_{3'},\end{aligned}$$

$$\frac{dN_3}{dt} = A_{3'3}N_{3'} - A_{31}N_3,$$

$$\frac{dN_4}{dt} = A_{3'4}N_{3'} - (A_{45} + A_{41})N_4,$$

$$\frac{dN_5}{dt} = A_{45}N_4 + W_{15}N_1 - W_{51}N_5,$$

$$N_0 = \sum_{n=1}^5 N_n,$$

where N_0 is the total molecular concentration. Solving this system of equations for the stationary case, we determine the population of the level 4:

$$N_4 = \frac{B_{12}N_0}{(A_{45} + A_{41}) \left(1 + \frac{B_{12} + A_{21}}{A_{23'}} \right) \left(1 + \frac{A_{3'3}}{A_{3'4}} \right) + B_{12} \left[1 + \frac{A_{45} + A_{41}}{A_{3'4}} \left(1 + \frac{A_{3'3}}{A_{31}} \right) + \frac{A_{45}}{W_{51}} \right]} \quad (1)$$

An analysis of this expression indicates that at a constant pumping rate the largest population of level 4 is reached for chelates with the following properties:

1. Low probability $A_{45} + A_{41}$, corresponding to long lifetime of the excited rare-earth ion state. This condition is fulfilled for practically all rare-earth chelates, whose lifetimes are of the order 0.5–1 μ sec for level 4.

2. High probability $A_{23'}$ of molecular transition to the triplet state, and low fluorescence probability A_{21} . This corresponds to the absence of fluorescence in the spectral region of the ligand.

3. Highly efficient energy transfer ($A_{3'4} > A_{3'3}$), which represents the absence or low intensity of ligand afterglow.

4. A low ratio $A_{3'3}/A_{31}$, representing a short lifetime for ligand afterglow. This means that ligand molecules are not accumulated at trapping levels.

5. Rapid depletion of the lower level in the laser transition, when W_{51} is large.

We are therefore most interested in laser utilization of chelates that do not luminesce in the spectral regions of ligand emission. Eu(BA) is an example. When ligand phosphorescence is present, chelates with weak or brief afterglow must be preferred.

Lasing by means of the 4 \rightarrow 5 transition requires that level 4 be sufficiently populated to make the gain at least as great as the loss when light traverses the length of the sample only once:

$$Kl \geq (1 - r), \quad (2)$$

where K is the gain, l is the length of the sample, and r is the reflection coefficient of the mirrors.

We shall now calculate the population N_4 required for laser action. We know that the gain is related to the concentration of excited atoms as follows:

$$K = \frac{n\Phi\lambda^4 A_{45}}{4\pi^2 c \Delta\lambda} \left(N_4 - \frac{g_5}{g_4} N_5 \right). \quad (3)$$

Here λ and $\Delta\lambda$ are the wavelength and half-width of the luminescence line, c is the velocity of light, n is the refractive index, g_4 and g_5 are the statistical weights of the working levels, and Φ is the fraction of molecules on level 4 that make radiative transitions to level 5. The population N_5 , which is proportional to $N_0 e^{-h\nu_{51}/kT}$, is found to equal $10^{-8} N_0$ for chelates with Eu at liquid nitrogen temperature; therefore N_5 can be neglected in the calculations. From (2) and (3) we then obtain

$$N_4 = \frac{4\pi^2 c \Delta\lambda (1-r)}{n\Phi\lambda^4 A_{45} l}.$$

Assuming $(1-r) = 5 \times 10^{-2}$, $l = 10$ cm, $n = 1.5$, $\lambda = 6130$ Å for chelates with Eu, $\Delta\lambda = 8$ Å, $1/A_{45} = 500$ μ sec, and $\Phi = 0.1$, we obtain $N_4 = 10^{17}$ molecules/cm³.

The pumping rate required to attain the aforementioned population of level 4 could be calculated exactly from (1). However, we are forced to use a cruder procedure because the probabilities $A_{3'3}$ and $A_{3'4}$ cannot be determined accurately by experimenters. The population of the excited level is obviously proportional to the number of quanta absorbed during the lifetime of the excited state:

$$N_4 = \eta \frac{Q\tau_4\alpha}{h\omega},$$

where Q is the pump power, τ_4 is the lifetime of the excited state, ω is the frequency of absorbed light, α is the absorption coefficient, and η is the luminescence quantum yield. We can thus determine the pump power. Chelates are characterized by an extremely high absorption coefficient α ; for a Eu(BA) solution with a concentration of 6×10^{18} molecules/cm³, $\alpha_{\max} = 1000$ cm⁻¹. Therefore only very thin layers of material can be excited at the absorption maximum. The entire volume of the amplifying medium is excited at the edge of the absorption band, where α is consider-

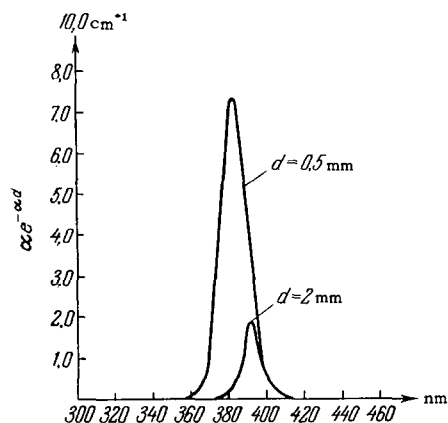


FIG. 7. Effective pump band of $\text{Eu}(\text{BA})_4$ solutions at different depths in sample.

ably smaller than at the maximum. The average value of α at the absorption edge for the aforementioned concentration is $\sim 50 \text{ cm}^{-1}$. Then, using $N_4 = 10 \text{ molecules/cm}^3$, $\omega \simeq 10^{15} \text{ sec}^{-1}$, $\eta = 0.8$, and $\tau = 500 \mu\text{sec}$, we obtain $Q = 3.3 \text{ W/cm}^2$.

The power requirement is thus obviously low and can be supplied by modern pulsed sources. However, the efficient utilization of wide-band pumping sources is hindered by the fact that the pump band of chelates is considerably narrower than the absorption band because of the high absorption coefficients. We shall determine in what spectral region the amplifying medium is excited at any given depth d . Consider a flux of radiation $F_0(\lambda)$ measured in W/cm^2 per unit interval of wavelength and impinging perpendicularly on the surface of the amplifying medium. The radiation flux absorbed at a depth d will be

$$F(\lambda) = \int_{\Delta\lambda} F_0(\lambda) \cdot \lambda \exp[-\alpha(\lambda) \cdot d] \alpha(\lambda) d\lambda.$$

We integrate over the entire absorption band. If $F_0(\lambda)$ is almost independent of wavelength in the absorption band we obtain

$$F(\lambda) = F_0(\lambda) \lambda_0 \int_{\Delta\lambda} \exp[-\alpha(\lambda) \cdot d] \alpha(\lambda) d\lambda.$$

Here λ_0 is the mean wavelength in the spectral region where the integral

$$R = \int_{\Delta\lambda} \exp[-\alpha(\lambda) \cdot d] \alpha(\lambda) d\lambda \quad (4)$$

does not vanish. In this spectral interval, which determines the effective pump band, the medium will be excited at some depth d . Figure 7 shows the dependence of the integrand in (4) on wavelength. The calculation employed the parameters $d = 0.5$ and 2 mm , and a concentration $6 \times 10^{18} \text{ molecules/cm}^3$ of the $\text{Eu}(\text{BA})$ solution. We observe that with increasing depth of penetration the peak of the effective pump band is shifted towards longer wavelengths and R is reduced sharply. The half-width of the "effective pump band" is $\sim 160 \text{ \AA}$.

We thus see that chelates are excited in actuality within a narrow spectral interval and that only a very small portion of the radiation from the pumping source is utilized. If we assume that the distribution of emission energy from pulsed lamps is close to the energy distribution in a blackbody spectrum at 7000° , then in the effective pump band (for a layer 2 mm thick) only 4% of the entire lamp energy is absorbed.^[16] A reduction of amplifying medium thickness improves the utilization of the pumping source. When working with chelates small-diameter resonators are therefore advantageous.

3. LASER ACTION IN CHELATES

To determine whether a particular chelate solution is suitable as the amplifying medium in a laser it is not sufficient to analyze its spectral properties alone. A solution with acceptable spectral properties must also satisfy the following requirements:

- 1) The number of active molecules must be sufficient to permit oscillation.
- 2) The solution must be optically homogeneous.
- 3) The solution must be photostable.

Optical homogeneity of the solution is easily achieved at room temperature. However, this condition creates a problem when the need for enhancing the luminescence yield leads to the requirement that the temperature of the solution be lowered considerably. The solvent must be vitrified at low temperatures, must be transparent in the long-wave region of pumping and emission, and must provide for high solubility of the chelate. Only a very limited number of solvents satisfy these requirements. A 3:1 mixture of ethyl and methyl alcohols is most frequently used in chelate lasers; sometimes dimethylformamide is added. At room temperature good results are obtained with acetonitrile as a solvent.

Strong pumping induces the photodisintegration of many compounds, such as those formed with picric acid. The luminescence intensity of the optically irradiated solutions declines sharply, so that these compounds cannot be utilized in lasers.

Laser action is usually achieved with the apparatus represented schematically in Fig. 8. Here 1 is the resonator containing the amplifying medium, 2 is a filter that passes the wavelengths required for pumping, 3 is a Dewar, 4 is a pulsed lamp, 5 is an illumi-

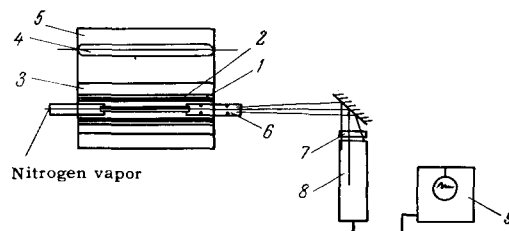


FIG. 8. Experimental scheme for achieving laser action in chelate solutions.

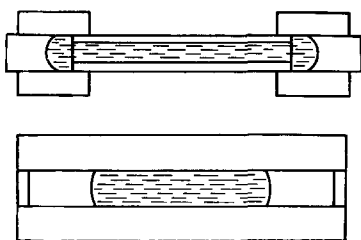


FIG. 9. Vessels used as resonators.

nator. 6 is the vessel holder, 7 is an interference filter isolating the wavelength at which oscillation is observed, 8 is a photomultiplier, and 9 is an oscillograph. The filter that discriminates the pumping region obviates undesirable heating of the solution that would result in the formation of bubbles and inhomogeneities. This filter also prevents absorption in the far ultraviolet region that would result in photodisintegration.

Small quartz vessels, 1–4 mm in diameter, are usually employed as resonators; their construction is shown in Fig. 9. The mirrors in these vessels are movable quartz pistons that are drawn into the vessel by surface tension as the cooled liquid contracts. The faces of these mirrors are spheres coated with a silver or dielectric reflecting layer. The radius of the spheres equals the length of the active layer; this makes the system confocal.

It is possible to evaluate experimentally the suitability of any selected medium and the efficiency of the apparatus by measuring the coefficient of negative absorption under specific experimental conditions.^[17] We know that the coefficient of negative absorption is related to the absolute brightness of luminescence by the formula

$$|K| = \frac{n\lambda^5 B_\lambda}{4\pi h c l}$$

Here B_λ is the absolute brightness of luminescence, n is the refractive index, l is the length of the sample, and λ is the luminescence wavelength.

The absolute brightness B_λ of luminescence can be determined by comparing the luminescence intensity with the brightness of a source having known absolute brightness at the same wavelength. The luminescence brightness is defined by

$$B_\lambda = B_{\lambda n} I \frac{t_1}{t_2},$$

where $B_{\lambda n}$ is the absolute brightness of the reference source at the investigated wavelength, I is the intensity at the luminescence line maximum as measured relative to the comparison source, t_1 is the exposure time for the emission spectrum belonging to the comparison source, and t_2 is the exposure time for the luminescence spectrum. Table I shows the results obtained with a number of alcohol solutions of chelates in apparatus that included a cylindrical illuminator and two IFK-2000 infrared lamps.

The described method was used experimentally to select the most promising chelates for lasers. Laser action in Eu-benzoylacetonate was observed for the first time in 1963.^[18] The alcohol solution was of 5×10^{18} molecules/cm³ concentration; its temperature was -150°C . The diameter of the active layer was 4 mm and its length was 50 mm. The oscillation threshold was 1900 J, which was about twice as high as the threshold for a ruby of the same diameter that is positioned between the same reflectors. When the jumping power was raised to 30% above the threshold the 6131-Å emission line was observed to narrow from 21 cm^{-1} to less than 0.5 cm^{-1} .

Laser action in Eu(BA) solutions prepared with piperidine was also reported in^[19]. Using thin layers of the solutions ($d = 0.8 \text{ mm}$) with a concentration of 10^{18} molecules/cm³, Schimitschek obtained a characteristic spike pattern and narrowing of the spectral line at about 650 J pumping power. We also have observed spiked oscillation in a frozen Eu(BA) solution inside a $d = 1 \text{ mm}$ capillary at 1200 J pump power.^[17] In^[9,10] lasing was reported in solutions of Eu(BA) with piperidine, morpholine, sodium, and diethylamine at low temperatures.

During the past two years several reports have been published concerning a certain irregularity of luminescence damping in the cases of Eu(TTA) and Tb(TTA) in a polymethylmethacrylate matrix.^[20–22] Increased pump power was accompanied by a reduction of luminescence duration and the appearance of additional maxima on the damping curve. The samples were polymer fibers ($l = 50 \text{ mm}$, $d = 0.25 \text{ mm}$). The authors attributed the modifications of the damping curve to stimulated emission. However, the experiments reported in^[23,24] cast doubt on this interpretation. It was found that similar irregularities are manifested by several chelates in cooled alcohol solutions but are not accompanied by the narrowing of the luminescence line that is characteristic of stimulated emission. These effects were observed in alcohol solutions of Eu(DBM)₃ and Eu(TTA)₃, and in Eu(BA) dissolved in an EPA mixture (ethanol, isopentane and ethyl ether in a 5:5:2 ratio), and were described in detail in^[25]. They are evidently associated not with oscillation, but rather with light absorption by excited molecules.

Table I

Medium	λ (Å)	Concentration of solution (mole/liter)	K (cm ⁻¹)
Eu(DBM) ₃ *	6154	10 ⁻³	1·10 ⁻³
Eu(BA) ₃	6131	10 ⁻³	8·10 ⁻⁴
Eu(EDSA) ₂ *	6169	10 ⁻⁴	1·10 ⁻⁴
Tb(DBM) ₃ *	5420	10 ⁻⁴	8·10 ⁻⁵
Tb(BA) ₃	5430	10 ⁻³	2·10 ⁻⁴
Sm(DBM) ₃	6454	10 ⁻³	2·10 ⁻⁶

* (DBM) – dibenzoylmethane, (EDSA) – ethylenediaminesalicylaldehyde.

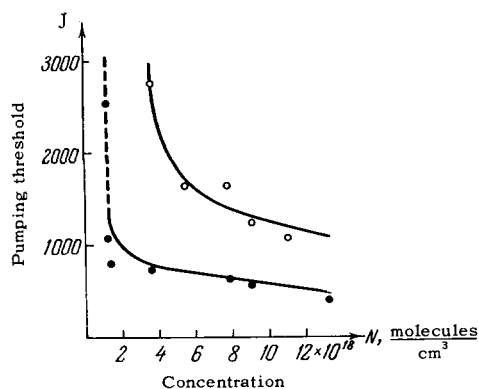


FIG. 10. Dependence of the laser threshold on the concentration of a Eu(BA) solution for different transmission coefficients of the mirrors: \circ - 6.6%; \bullet - 0.1%; vessel diameter 1 mm.^[28]

Laser action in a liquid chelate solution is especially interesting.^[26] Lasing has been observed in a solution of Eu-benzoyltrifluoroacetate $\text{Eu}(\text{BTA})_4$ in acetonitrile at room temperature. Work with a vessel of 1-mm diameter yielded oscillograms exhibiting typical laser spikes and narrowing of the 6119-Å line from 34 to 0.3 Å. The threshold was 1700 J. Until very recently only solids and gases exhibited laser action. Liquid lasers provide an extremely attractive prospect, since they make it possible to combine high concentrations of active molecules with circulatory motion that eliminates undesired heating of the amplifying medium.* This type of laser was recently constructed by Schimitschek et al.^[31] A solution of Eu-ortho-chlorobenzoyltrifluoroacetate in acetonitrile was circulated inside of the resonator at 100 cm/sec in a temperature of +10°C. The energy required for the circulation raised the threshold only 7%.

The investigation of chelate laser properties is of great interest because here for the first time the properties of liquid systems with population inversion is being discussed. It was doubted at one time that a viscous medium could oscillate because of the temperature gradient of the refractive index that is set up through the thickness of the sample when pumping commences.^[27] Experiment shows, however, that losses associated with this effect do not prevent oscillation. The loss during one passage of light is evaluated at 10–25%. The energy output of chelate lasers is still small. Thus, for Eu(BA) lasers the output is 1 J from vessels with 1–4-mm diameters.^[28]

The properties of emission from cooled liquid systems are very similar, in general, to the properties of solid-state laser emission, although a certain influence of the particular solutions is manifested.^[28] The anomalously high absorption by the chelates leads to

*In August, 1966 Lemicki and Heller reported a new form of liquid laser with $\text{Nd}^{3+}:\text{SeOCl}_2$ as the amplifying medium.^[32] The energy output of this laser is comparable with that of the best solid-state lasers.

strong dependence of the observed laser threshold on the thickness of the amplifying-medium layer. For example, for a Eu(BA) solution in a vessel of 1-mm diameter the threshold is 650 J; for $d = 4.7$ mm the threshold is 1250 J. The dependence of the threshold on the concentration of active molecules is less pronounced. Increased concentration above a certain critical value leads to a very slow reduction of the threshold (Fig. 10). This behavior of the concentration dependence agrees with the calculation of the effective pump band as a function of the concentration.^[16] The critical region of concentrations below which laser action does not occur is determined by the transmission coefficient of the mirrors. Thus, for a vessel of 1-mm diameter with transmission $(1-r) = 6.6\%$ this region of N_{Cr} corresponds to 3.4×10^{18} molecules/cm³; with $(1-r) = 1\%$, $N_{\text{Cr}} = 1.1 \times 10^{18}$ molecules/cm³. In more dilute solutions oscillation does not begin at power below 3000 J.

The thickness of the amplifying layer determines the character of the laser spikes. In a vessel with $d = 1$ mm and spherical mirrors disordered spikes are observed (Fig. 11). In vessels with $d = 4.7$ mm the character of the spikes is different; at certain time intervals regular undamped spikes appear. This regularity usually accompanies the appearance of one or more longitudinal modes. However, the diffuseness of the Fabry-Perot interferograms shows that some transverse modes can also be produced.

The experimental investigation of vibrational modes in liquid lasers is hindered by the fact that their design does not permit retesting with merely a change of the solution. In ^[28] it was established, by exciting a single identical sample in a vessel of 1-mm diameter, that a strong axial mode sometimes results. In other instances the radiation was concentrated in a circle close to the walls of the vessel or at isolated points. This distribution was attributed by the same investigators to either a set of longitudinal and transverse modes, or to a high-order cylindrical mode. Interferograms registered for a vessel with 1-mm diameter showed the presence of four components having frequencies that differed by 0.06 cm^{-1} ; these corresponded to different longitudinal modes.

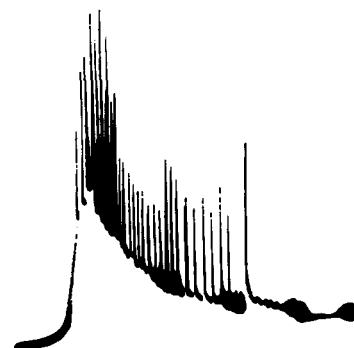


FIG. 11. Oscillogram of Eu(BA) solution in vessel of 1.4-mm diameter. Pump power $Q = 1200 \text{ J}$.^[17]

Table II

Medium	Solvent	$t, ^\circ\text{C}$	Oscillation threshold
Eu(BA) ₄ with piperidine	ethanol-methanol (3:1)	-150°	100 J ^[29]
Eu(BA) ₄ with ammonia	ethanol-methanol (3:1)	-150	280 J ^[29]
Eu(BTA) ₄ with piperidine	acetonitrile	+25	1700 J ^[26]
Eu-trifluoroacetylacetonate with ammonia	ethanol-methanol (3:1)	-150	670 J ^[29]
Eu(BA) ₄ with diethylamine	ethanol, methanol	-140	- ^[9]
Eu(BA) ₄ with morpholine	ethanol, methanol	-140	- ^[9]
Eu(BA) ₄ with Na	ethanol-methanol-dimethylformamide (15:5:2)	-140	1000 J ^[10]
Eu(DBM) ₄	ethanol, methanol plus some dimethylformamide	-140	- ^[30]

The foregoing data on the properties of the emitted radiation pertain to solutions of Eu(BA). Other chelates were not subjected to similar study, although the existence of laser action was established for many organometallic complexes. Table II contains a list of oscillating rare-earth chelates and the conditions for emission (the solvent, temperature, and minimum oscillation threshold).

It should not be assumed that these chelates possess the properties of optimal lasers. An unusually high absorption coefficient makes it necessary to work with a high level of pump power and at the same time with thin layers of the medium that do not yield very much emission power.

At the present time work is being done on the synthesis of chelates with a lower absorption coefficient of the ligand and with higher efficiency of energy transfer from the ligand to the rare-earth ion; solvents ensuring a high luminescence yield are being investigated. Numerous publications show that it is still possible to increase the number of lasing chelates.

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