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Spectroscopy and Luminescence Properties of CdF_2:Eu

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Characteristics relevant to the application of $CdF_2:Eu^{+3}$ to optical maser use were investigated. The line fluorescence was analyzed to obtain the positions of the lowest energy europium crystal states and these were found to be consistent with the europium ion being in a crystal field having essentially tetragonal symmetry. The strongest emission line, at 5893.1 A, contains $\frac{1}{10}$ of the total fluorescence and is due to a transition between states at 17278.6 cm^{-1} and 309.7 cm^{-1}. At 15°K its width at half intensity is 0.32 cm^{-1}. It was found that the europium fluorescence could be sensitized by the addition of sulfide to the crystals and the total fluorescent quantum efficiency was determined to be 0.8 ± 0.2. The threshold power for oscillations in a rod of 0.1 cm^2 cross-sectional area was calculated to be 18 watts.

INTRODUCTION

To develop a solid material suitable for observing stimulated emission at visible wavelengths, essentially two fundamental criteria must be met, as has been shown by Schawlow and Townes.[1,2] First, the solid must efficiently absorb energy from an external "power supply" (such as a pumping lamp) and convert it into an extremely narrow emission line, losing as little energy as possible in other fluorescent emission or nonradiative processes. Second, the optical properties of the material must be such that this narrow fluorescent emission can build up a relatively high radiation density within the material. If oscillations are to be observed in the steady state, then in addition to these criteria, the lifetimes of the various energy levels involved must be in the correct ratios.

We present here the results of an investigation of cadmium fluoride activated with trivalent europium in which most of the characteristics relevant to the above criteria have been explored. In particular, we discuss the energy level scheme of the europium ion as deduced from the emission spectra, the total fluorescent quantum efficiency, the fraction of the fluorescence in the strongest line and the width of the strongest emission line. The first of these was investigated so as to determine the suitability of CdF_2:Eu as a 4-level optical maser and the other properties determine the pumping power needed for oscillations.

It will be shown that the energy level scheme also gives us information on the nature of the charge compensation which occurs in CdF_2:Eu. Our results will be compared with those obtained from paramagnetic resonance studies by other investigators on rare earths in calcium fluoride, which has the same structure as CdF_2.[3-5] To our knowledge there have been no other analyses of the spectra of rare earth ions imbedded as impurities in host crystals, except when they replace cations in the same valence state, which are sufficiently complete to allow deductions concerning the symmetry of the rare earth's environment. There are, however, a number of complete analyses of the spectra of several europium salts and these will be useful for interpreting our results.[6-8]

We will also present here preliminary results on the sensitization of CdF_2:Eu with sulfide.

EXPERIMENTAL PROCEDURE

Large crystals of CdF_2 were grown from powder, supplied by the General Electric Chemical Products plant, by the Bridgeman technique as has already been described elsewhere.[9] The activator was added as EuF_3 in concentrations between 10^{-5} and 10^{-1} mole fraction. The sensitizer, when used, was added as CdS. Pieces suitable for absorption and emission studies were cut from the boules, polished, and mounted in a Hofman D-1930 double vessel stainless steel cryostat. The spectra were measured at a variety of temperatures between 15° and 370°K but the results to be presented here will largely be those obtained at 25°K. In the emission measurements, the crystals were excited with the radiation from a C3H85 G.E. mercury arc lamp filtered by a Corning 9863 color glass filter.

Absorption was measured with a Cary model 14 double beam recording spectrophotometer. Emission spectra were recorded photoelectrically with a 0.5-meter Jarrell-Ash grating spectrometer (model 82-000) and on a 2-meter Bausch and Lomb dual grating spectrograph. The spectra were also recorded photographically on the latter instrument.

RESULTS AND DISCUSSION

Line Emission and Absorption Spectra

Figure 1(a) is a photoelectric recording of the strongest emission lines. Figure 1(b) is a recording which

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[1] A. L. Schawlow and C. H. Townes, Phys. Rev. **112**, 1940 (1958).

[2] A. L. Schawlow, The S. S. Journal **2**, 21 (1961).

[3] B. Bleaney, P. Llewellyn, and D. Jones, Proc. Phys. Soc. (London) **B69**, 858 (1956).

[4] J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

[5] E. Friedmann and W. Low, J. Chem. Phys. **33**, 1275 (1960).

[6] E. V. Sayre and S. Freed, J. Chem. Phys. **24**, 1211 (1956).

[7] K. H. Hellwege and H. G. Kahle, Z. Physik **129**, 62 (1961).

[8] G. Dieke, H. Crosswhite, and B. Dunn, J. Opt. Soc. Am. **51**, 820 (1961).

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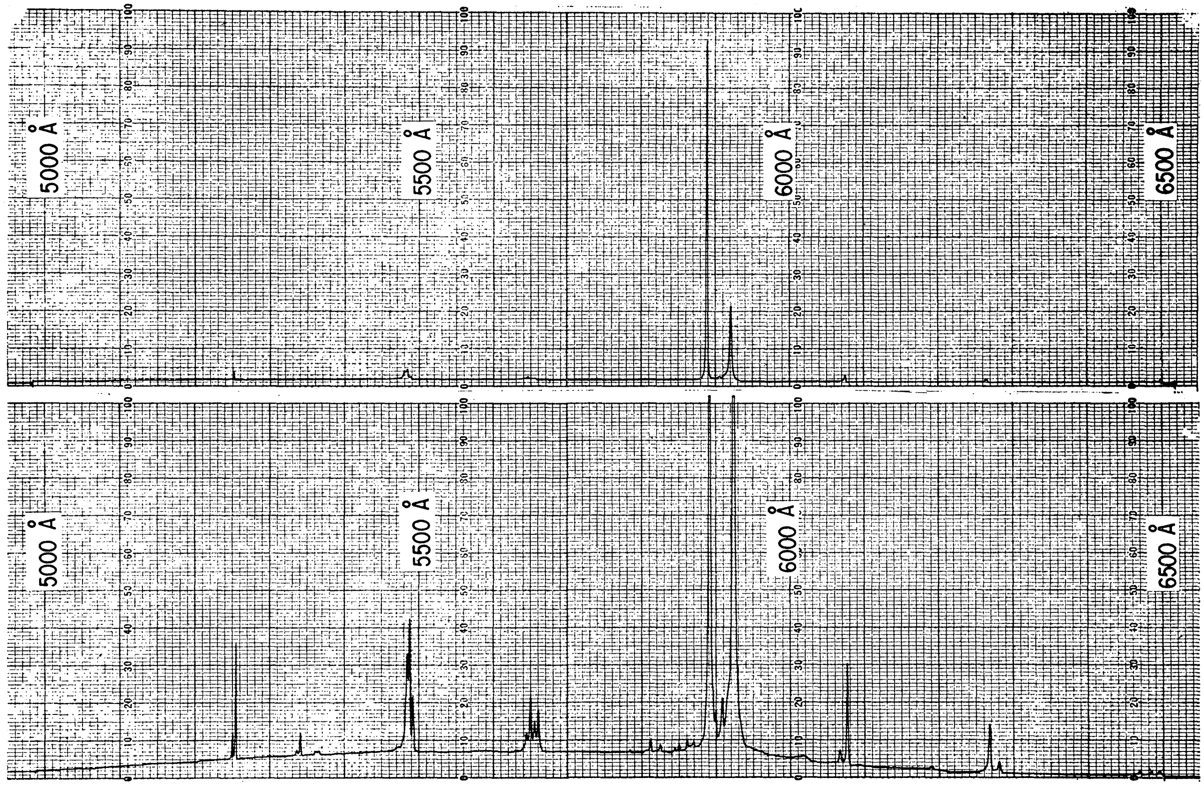

FIG. 1. (a) (upper) A photoelectric recording of the strongest emission lines of CdF_2:Eu. (b) (lower) A photoelectric recording over the same wavelength range as above but with the sensitivity increased 10 times.

covers the same wavelength range as Fig. 1(a) but the sensitivity has been increased 10 times to show the weaker lines. These figures show that the strongest line at 5893.1A is four times as intense as the line at 5924.7A and 25 or more times as intense as any of the remaining lines. Correcting for the wavelength dependence of the detection system does not alter this conclusion. The emission which appears to be a single line in Fig. 1(a) is actually two lines at 5892.3A and 5893.1A, both having about twice the intensity of the 5924.7 A line.

We have observed a total of about 80 emission lines with wavelengths ranging from 5251 to 8150 A and we estimate from the number and intensities of these that about $\frac{1}{8}$ of the line emission appears as the strongest line. The broad band emission discernible in Fig. 1(b) has an intensity about $\frac{1}{4}$ of the total line intensity so that the 5893.1-A line has about $\frac{1}{10}$ of the entire fluorescent intensity and we can place an upper limit of $\frac{1}{10}$ on the quantum efficiency for exciting this line.

The effectiveness of a 4-level maser requires that the terminal state of the stimulated transition is separated from the ground state by an energy greater than kT. The position in energy of the terminal state of the 5893.1-A emission line of CdF_2:Eu is thus relevant to the application of this material to optical maser use. An examination of the term scheme of Eu^{+3} indicates that the 5893.1 A transition might occur between crystal states derived from the $^5D_0$ and $^7F_1$ or $^5D_1$ and $^7F_3$ free ion states. In the former case, the terminal state would lie about 350 cm^{-1} above the ground state and in the latter case it would be at approximately 1900 cm^{-1}. If the terminal state is separated from the ground state by 350 cm^{-1}, sufficient depopulation of this state would occur only at liquid nitrogen temperature, while states near 1900 cm^{-1} are essentially unpopulated at room temperature.

In order that we might determine the separation of the terminal state of the 5893.1-A emission of CdF_2:Eu from the ground state, the line absorption spectrum was measured as a function of temperature and the emission and absorption spectra were analyzed to deduce the energy level scheme.

The oscillator strengths for all of the lower energy transitions of Eu^{+3} (those between the ^7F and ^5D states) are extremely small. To observe the line absorption we found it necessary to grow a crystal containing 10 mole % europium. Unfortunately the emission spectrum of this crystal differed from the spectra of crystals containing smaller amounts of activator, presumably because of the interaction of paired europium ions. As well as broadening the emission lines considerably, new lines appeared and the relative intensities were somewhat altered. The spectra were, however, sufficiently

TABLE I. Absorption lines observed at 300° and 85°K.

T(°K)	Observed absorption lines (A)				
300	5924.7	5893.1	5787.5	5342.3	5255.9
85			5787.5		5255.9

similar that we were able to obtain important hints as to the states involved in several of the transitions.

Table I shows groups of absorption lines which were observed at 300°K and 85°K in a 1.5 cm^{-1} thick piece of CdF_2:0.10Eu. It is seen in Table I that the 5924.7-, 5893.1-, and 5342.3-A lines disappear on cooling while the 5787.5- and 5255.9-A lines remain, implying that the former set of absorption lines initiate in states other than the ground state while the latter involve excitation of ions initially in their lowest energy state. The energy differences between 5787.5 and 5893.1 A as well as between 5255.9 and 5342.3 are approximately 310 cm^{-1}.

The line absorption was measured at several temperatures between 85° and 300°K and the temperature dependence of the 5893.1- and 5342.3-A lines was consistent with the assumption that these transitions occur from a state about 310 cm^{-1} above the ground state.

The 5787.5- and 5255.9-A absorption lines evidently occur from the ground state to levels at 17278.6 cm^{-1} and 19026 cm^{-1}. Comparison with the results obtained on europium salts shows that these levels are those derived from free-ion states usually labeled $^5D_0$ and $^5D_1$.

Other absorption lines at wavelengths less than 5250 A were also observed but these were not studied because no fluorescence was observed which might originate in these higher states and the crystal Stark splittings could be studied only at low europium concentrations, thus only in fluorescence.

Analysis of the Fluorescence Spectrum

With the hints gained from the absorption spectrum, the deduction of the term scheme becomes relatively straightforward, once reasonably accurate values for the wavelengths are obtained. There is, however, one difficulty encountered in the analysis of rare earth activated phosphors which does not occur in studies of rare earth salts. The rare-earth ion in the salt has a unique local environment so that a unique energy level scheme results. A rare-earth ion imbedded in a host lattice may, however, find itself in one of several symmetries due to the several ways in which other defects may be associated with it. If a number of these various distinct luminescent centers are present, the analysis is considerably more difficult. We have found more than one type of center in CdF_2:Eu but it is possible to enhance the emission of one of these considerably through careful preparation.

The emission line at 5787.5 A is quite sharp, very weak, and there is no evidence of Stark splitting. As we shall see, this line is due to transitions between A_1 crystal states which are derived from the $^5D_0$ and $^7F_0$ free ion states. There are two lines at approximately 5250 A; one of these is at 5255.9 A and the other is at 5251.5 A. Thus fluorescence occurs from states at 17278.6 cm^{-1}, 19026.0 cm^{-1}, and 19042.0 cm^{-1} so that the spectrum consists of three series of lines. Two of these series are separated by only 16 cm^{-1}, so for every group of lines resulting from transitions from the state

TABLE II. Identified emission lines as observed at 25°K—arranged by series.

1st series		2nd series		3rd series		Position of crystal state in cm^{-1}
λ_1(A)	$17278.6-10^8/\lambda_1$	λ_2(A)	$19026.0-10^8/\lambda_2$	λ_3(A)	$19042.0-10^8/\lambda_3$	
5787.5	0	5255.9	0	5251.5	0	0
5902.34	307.4	5342.3	307.5	5337.2	305.6	307.4
5893.14	309.7	...	...	5337.9	308.1	309.7
5924.7	400.1	5368.8	399.9	5363.5	397.5	400
6067.8	798.2	5486.3	798.8	...	...	798
6077.9	825.5	5494.9	827.3	5489.1	824.1	826
6271.1	1332.4	5654.2	1340.0	5648.0	1336.7	1334
6284.5	1366.4	5665.5	1374.3	5659.6	1372.9	1368
6471.1	1825.3	5814.6	1827.9	5808.7	1826.4	1826
6487.3	1863.9	5827.3	1863.4	5821.5	1864.3	1864
6498.9	1891.4	5836.5	1892.4	5831.0	1892.3	1892
6519.1	1939.1	5852.6	1939.6	5847.1	1939.5	1939
6534.0	1974.0	5864.5	1974.2	5858.4	1972.5	1974
6545.2	2000.2	5873.5	2000.4	5868.0	2000.4	2000
6906.0	2798.4	6163.0	2800.1	...	...	2799
6947.5	2884.9	6195.0	2883.9	...	...	2885.0
6949.2	2888.5	6196.3	2887.3	6190.2	2887.4	2888.6
6956.5	2903.1	6202.4	2903.2	...	...	2903
7050.3	3094.8	6276.4	3093.3	...	...	3094
7054.2	3102.6	6280.1	3102.7	...	...	3103
7107.7	3209.4	6322.0	3208.2	...	...	3209
7414.0	3790.6	6563.9	3791.2	6556.4	3789.7	3791
7418.1	3798.2	6567.8	3800.2	6560.3	3798.8	3799
8125	4970.9	7114.4	4970.0	...	...	4970
8150	5008.7	7133.1	8006.8	...	...	5007

at 17278.6 cm^{-1} there is a group of lines with twice as many components at shorter wavelengths. This is illustrated in Fig. 2 for the lines which terminate in states at 1334 cm^{-1} and 1368 cm^{-1}.

Table II lists all of the observed lines which could be identified as emission from one center. A line was assigned to the dominant center only if there was a second line differing from the first by 1747 cm^{-1} or 1763 cm^{-1}. In this way we have located 24 crystal states which apparently arise from the 7 components of the ^7F ground state multiplet of the free ion. Fluorescence was observed from all 3 of the states at 17278.6 cm^{-1}, 19026 cm^{-1}, and 19042 cm^{-1} to 15 of these lower energy states.

In addition to the 63 emission lines listed in Table II, approximately 20 other lines have been observed but could not be assigned to any one center. About half of these spurious lines lie in the spectral range 5880 to 5950 A, that is, near the strong 5893.1- and 5924.7-A lines of the dominant center. These probably arise from centers similar, but not identical to the center which is most prevalent in the crystal. Most of the remaining unidentified lines lie between 6500 and 7100 A. Many of these may result from transitions from the state at 19026 cm^{-1} to states in the range 3700 cm^{-1} to 5000 cm^{-1}. The transitions to these same states from the 17278.6 cm^{-1} energy level are quite weak and lie between 7400 and 8000 A where the sensitivity of detectors is lower than that available in the visible region of the spectrum.

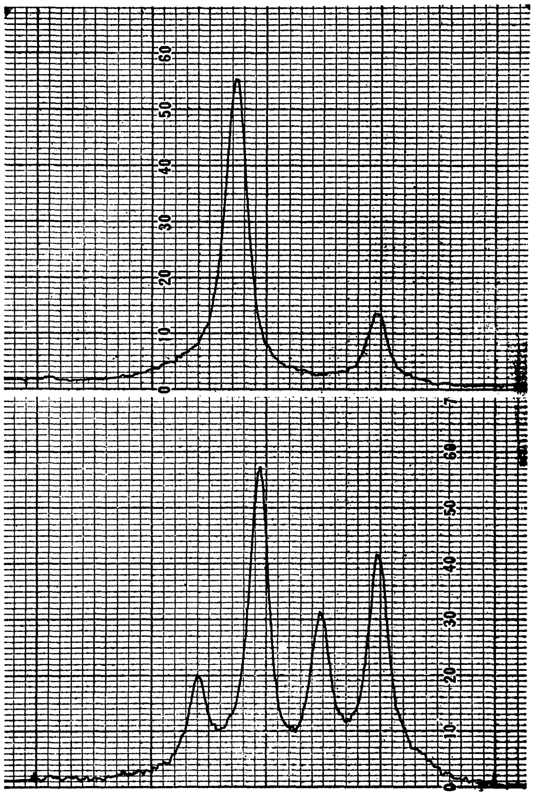

FIG. 2. The upper recording shows the emission lines resulting from transitions between the state at 17278.6 cm^{-1} and the states at 1334 cm^{-1} and 1368 cm^{-1}. The lower recording shows the emission lines from the states at 19026 cm^{-1} and 19042 cm^{-1} to the states at 1334 cm^{-1} and 1368 cm^{-1}.

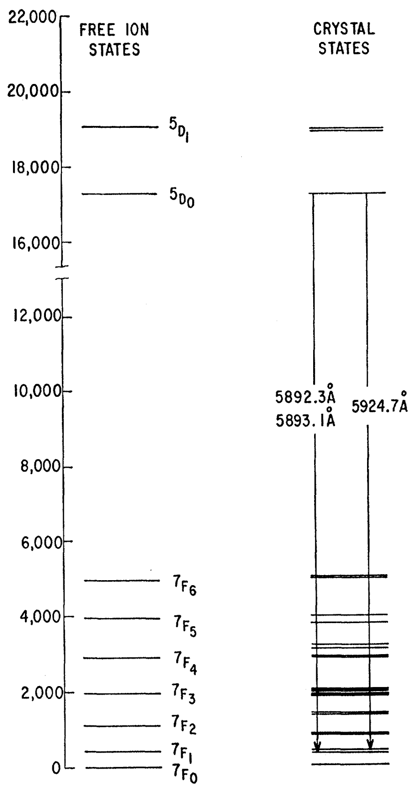

FIG. 3. The states of the Eu^{+3} ion as deduced from the emission spectra.

The results of the spectral analysis are shown in Fig. 3. Some of the states in Table 2 are spaced too closely to show as separate levels in Fig. 3 so the lowest 20 levels are shown in Fig. 4 in greater detail. The levels in Figs. 3 and 4 which are labeled as free ion states are the approximate positions of the free Eu^{+3} ion levels as deduced from the spectra of several europium salts.[6–8] The crystal states shown in Fig. 4 have been grouped together purely on the basis of position in energy to show the apparent free ion parentage of the various crystal states. Table III summarizes the observed splittings and includes the number of states expected for local fields of various symmetries.[10] The splitting of the level at 308 cm^{-1} into levels separated by 2.3 cm^{-1} and the splitting of the level at 2887 cm^{-1} into levels separated by 3.6 cm^{-1} have been ignored in Table III because these separations are significantly smaller than the other splittings.

To a first approximation the Stark splittings of the

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[10] H. A. Bethe, Ann. Physik 3, 133 (1929).

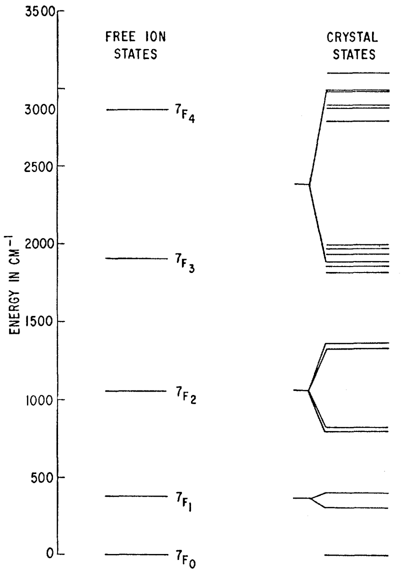

Fig. 4. The lowest 20 levels of the Eu ion.

$^7F_1$, $^7F_2$ and $^5D_1$ states imply that the europium ion is in a field of tetragonal symmetry. Since the $^7F_1$ state actually splits into 3 states there must be deviations from perfect tetragonal symmetry, as required by the Jahn-Teller theorem.[11] Most of the lines are too broad for splittings of the order of 2 cm^{-1} to be resolved but the 5892.3-, 5893.1-, 6947.5- and 6949.2-A lines are particularly sharp.

The splittings of the $^7F_3$ and $^7F_4$ states which are given in Table III do not agree with the group-theoretical calculations for tetragonal symmetry. This may be, in part, due to the inclusion of a state in the $^7F_3$ group which does not belong to the dominant center. This seems unlikely, however, since fluorescent lines from all 3 "initial" states to all 6 terminal states have been observed. The extra line in this group may arise because of the deviations from perfect tetragonality but the smallest separation in the $^7F_3$ group is 26.2 cm^{-1} or about 10 times as large as the splitting of the 5893.1-A lines. Perhaps only 6 states of the $^7F_4$ group were observed because transitions to the seventh state were too weak.

Since the sum of the number of states in the range 1820 cm^{-1} to 3210 cm^{-1} is 12, the correct number for tetragonal symmetry, it is conceivable that one of the 6 states in the group centered about 1900 cm^{-1} is actually split off from the $^7F_4$ free ion state. That is, the crystal field may be strong enough to cause appreciable mixing of the $^7F_3$ and $^7F_4$ free ion states. The structure of the group of states arising from the $^7F_2$ state indicates that the Stark splitting is quite large since the over-all splitting of this group is 570 cm^{-1} while the free-ion spin-orbit splitting ranges from 370 cm^{-1} to 1000 cm^{-1}.

Only four states were found which seem to be derived from the $^7F_5$ and $^7F_6$ free ion states. The remaining crystal states of these groups could not be identified primarily because of lack of detector sensitivity at wavelengths greater than 6500 A.

If we are correct in concluding that the Eu^{+3} ion experiences a crystal field having tetragonal symmetry, then our results are in agreement with those of Bleaney, Llewellyn, and Jones for the system CaF$_2$:Nd^{+3}.[3] These investigators interpreted their paramagnetic resonance spectra as implying that the Nd^{+3} ion substituted for a calcium ion and the symmetry was reduced to tetragonal because of an association of an interstitial fluorine ion along a $\langle 100 \rangle$ direction. If the neodymium site is (0,0,0) the interstitial fluoride ion is at one of the six equivalent ($\frac{1}{2}$,0,0) sites.

If the charge compensating defect were either a cation vacancy or a substitutional monovalent cation, association with the rare earth ion would result in C_{2v} symmetry and a complete lifting of all degeneracy into $2J+1$ states. If there were divalent anions substituting for fluoride ions, these would associate along $\langle 111 \rangle$ axes, placing the rare earth in an electric field having C_{3v} symmetry. This is a hexagonal group and the expected energy level structure is given in Table III. If no association with the rare earth occurs, then the splitting will be that of cubic symmetry.

We attempted to obtain additional evidence that the structure of the fluorescent center is as described above, through observation of a polarization of the emission lines. Polarizing prisms were placed between the exciting lamp and the crystal and polaroid filters between the crystal and monochromator. No significant polarization was found, however. This may be a consequence of the lack of a dichroic absorption in the excitation band or because the polarization is not preserved in the transfer of the energy from the center which absorbs the excitation to the center which emits the fluorescence. No attempt was made to excite directly in the line absorption of the activator ion.

Other Centers

Various investigators have observed the paramagnetic resonance of trivalent cations in CaF$_2$ at sites having cubic or hexagonal symmetry.[5,12] The cubic

Table III. The number of crystal states arising from the various free europium ion states and the numbers expected for various symmetries.

$J=$	0	1	2	3	4	5	6
CdF$_2$:Eu	1	2	4	6	6	2	2
Cubic	1	1	2	3	4	4	6
Hexagonal	1	2	3	5	6	7	9
Tetragonal	1	2	4	5	7	8	10
Lower symmetry	1	3	5	7	9	11	13

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[11] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A164**, 117 (1937).

[12] J. Sierro, J. Chem. Phys. **34**, 2183 (1961).

symmetry can occur, apparently, when the compensating defect has a mobility much smaller than that of the fluorine interstitial, so that association does not occur. The work of Sierro[12] and that of Friedman and Low[5] indicate that this compensating ion is a divalent oxygen ion substituting at a fluoride lattice site.

Feofilov discovered that the fluorescence of CaF$_2$:Eu was polarized along a $\langle 111 \rangle$ direction, which he interpreted as implying an association of an oxygen ion with the rare earth.[13] Sierro[12] studied the paramagnetic resonance spectra of CaF$_2$:Gd^{+3} crystals which had been heated in water vapor. He found gadolinium ions at sites having cubic, tetragonal, and hexagonal symmetries.

We have observed a second fluorescence spectrum in CdF$_2$:Eu which we believe to be caused by replacement of the fluorine interstitial compensation with substitutional oxygen compensation. This second spectrum differs significantly from the spectrum described in Table 2 with respect to the line intensities and Stark splittings. Feofilov and Stepanov[14] have observed similar, but not identical, behavior for rare earths in CaF$_2$.

The crystals which show this second spectrum were grown with CdO added to the melt. Also, the spectrum already described could be partially converted to the second spectrum by heating the crystals to 1000°C for 20 hours in an argon atmosphere containing water vapor at a pressure of 10^{-2} mm Hg.

Because we have not yet obtained crystals in which the second type of spectrum dominates over other emission sufficiently, we have made only a preliminary analysis of this spectrum. The results thus far obtained indicate that the $^7F_0$, $^7F_1$, $^7F_2$ and $^7F_3$ free-ion states split into 1, 1, 2 and 3 crystal states respectively, which would imply cubic symmetry.

Friedman and Low[5] suggested that the cubic spectrum could be obtained by quenching the CaF$_2$:Gd crystals from temperatures near 1200°C. We have quenched CdF$_2$:Eu from the melt to room temperature and from 1000°C to room temperature in about 2 minutes but obtained only the tetragonal spectrum as long as there was no oxygen present.

Linewidth

The pumping power required to initiate oscillations in a 4-level optical maser is proportional to the width of the spontaneous emission line.[1,2] So that the necessary power might be determined for the case of CdF$_2$:Eu the separation of the half-intensity points of the 5893.1-A emission line was measured as a function of temperature. The results are shown in Fig. 5. It has already been mentioned that this consists of two lines separated by approximately 0.8 A but above 100°K the emission from these two lines overlap and they cannot be resolved. In the temperature range from 100°K to 178°K the value shown in Fig. 5 is the overall width of the two partially overlapping lines. Above 175°K the emission is essentially one Gaussian curve. In the temperature range from 15° to 100°K the width of the more narrow of the two lines is shown, the second line being about 10% wider. At 15°K the width of the narrowest line was 0.11A (0.32 cm^{-1}) and it appears from Fig. 5 that cooling the crystal to lower temperatures would yield still smaller half-widths.

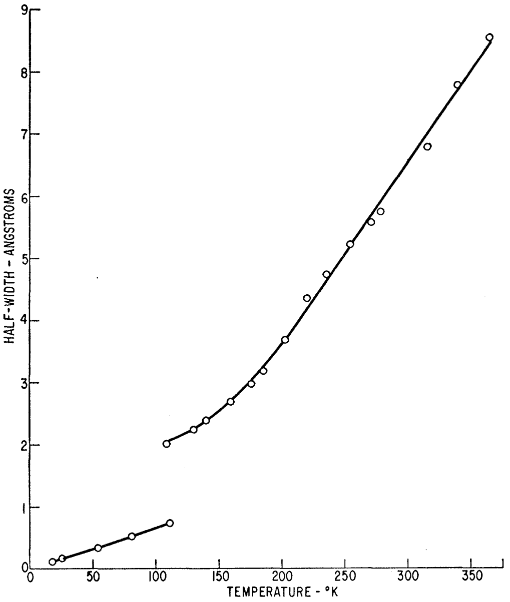

FIG. 5. The half-width of the 5893.1-A emission line as a function of temperature.

The data shown in Fig. 5 were obtained with crystals having europium concentrations of 10^{-4} and 10^{-3} mole fraction. The only differences between these two concentrations was that the 10^{-3} mole fraction crystals showed slightly greater half-widths at the lowest temperatures. Significantly larger half-widths were found in crystals containing 1% or more europium.

Fluorescence Sensitization and the Excitation Spectrum

If the CdF$_2$:Eu powder is carefully purified and the crystals are grown in pure argon, very little optical absorption is found other than the characteristic host absorption. If one is to utilize the radiation from a pumping lamp efficiently, an optical maser material must have absorption coefficients of the order of several cm^{-1} in the spectral regions where strong emission from the lamp occurs.

We have found that the addition of CdS to the crystals of CdF$_2$:Eu produces an absorption band whose maximum occurs at 2830A. This absorption is found only when both sulfur and europium are present.

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[13] P. P. Feofilov, Doklady Akad. Nauk SSSR **99**, 731 (1954).

[14] I. V. Stepanov and P. P. Feofilov, Soviet Phys.—Doklady **1**, 350 (1956).

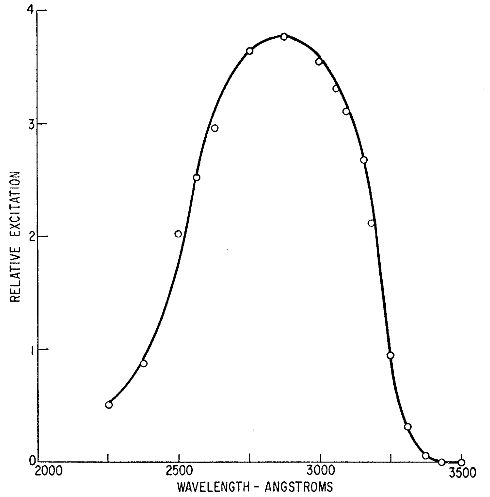

FIG. 6. The excitation spectrum of CdF_2:Eu,S. The crystal thickness is 1 cm. The quotient, fluorescence intensity/excitation intensity, is plotted as a function of wavelength.

Radiation absorbed in this band excites a fluorescence identical to that from the crystals containing no sulfur. We are currently extending our investigations of the sensitization process but the available results point to the following hypothesis: A large fraction of the added sulfide substitutes for fluoride ions in nearest neighbor positions to the europium ions but leaves other europium ions associated with fluoride ions. The europium-sulfide ion pairs produce an absorption band at 2830A, probably as a consequence of the excitation of outer shell sulfide ion electrons. After being excited, the europium-sulfide ion pair relaxes into an energy state which may be considered as essentially an excitation within the $4f^6$ configuration of the europium ion. The states of this excited europium ion are similar but not identical to those of a europium ion associated with a fluoride ion. The difference between the two types of europium ions is small enough that radiationless energy transfer can occur between them and as a consequence the europium-sulfide ion pair de-excites and the europium-fluoride ion pair becomes excited.

We hope to test this hypothesis with further experiments. An excitation spectrum obtained in crystals sensitized with sulfur is shown in Fig. 6.

Quantum Efficiency

The accurate measurement of the fluorescent quantum efficiency of single-crystal phosphors is rather difficult. The emission pattern of the fluorescence is dependent on the shape of the crystal, the penetration depth of the radiation, the index of refraction of the material and the condition of the crystal surfaces.

In our measurement the crystal was a right circular cylinder and the monochromatic excitation was incident along the cylinder axis upon a small area in the center of one of the flat polished surfaces. The fluorescence was measured with a calibrated trialkali photocell at right angles to the incident beam and compared with its intensity. Since the experiment was arranged such that there was essentially cylindrical symmetry about the axis of the sample, the radiation pattern could be determined by measuring the fluorescent intensity in only one plane containing the symmetry axis.

The quantum efficiency at 80°K for radiation absorbed in the sulfur-europium band was determined to be 0.8±0.2. It was also determined that about $\frac{1}{4}$ of the total emission appears in the 3 most intense lines (the $^5D_0$ to $^7F_1$ transitions). Since the two strongest lines are both twice as intense as the next most intense line, $\frac{1}{10}$ of the fluorescence appears in each of the most intense lines in agreement with an estimate given earlier.

The fraction of the fluorescence appearing in one line may also be calculated if the decay time of the luminescence and the absorption strength of line in question are known. Assume that there is only one state from which fluorescence occurs and the lifetimes for transitions to the various lower states are called τ_j. Then the fluorescent decay time is $\tau_0=1/\sum_j (1/\tau_j)$, and the intensity in the jth transition is $I_j=n_i/\tau_j$ so that the fraction of the fluorescence in the jth emission line is $(1/\tau_j)/\sum_i (1/\tau_i)$. It may be shown that for absorption from a state j to the fluorescent excited state x,

$$\alpha_{jx}=\frac{1}{\Delta\nu_{jx}}\frac{(\ln 2)^{\frac{1}{2}}}{4\pi^{\frac{3}{2}}}\lambda_0{}^2\frac{g_x}{g_j}\frac{(N_j-N_x)}{\tau_j},$$

so that by measuring the values α_{jx} (the absorption coefficient in cm^{-1}), $\Delta\nu_j$ (the linewidth in cycles/sec), λ(the wavelength in cm), g_x and g_j (the statistical weights of the excited and initial states) and N_j-N_x (the difference in populations) we may calculate τ_j. Using the data obtained with the 1.5-cm CdF_2:0.10Eu crystal, we calculate a lifetime for the transition corresponding to the 5893.1-A line of 0.08 sec. The measured fluorescent decay time was 0.010 sec. Recalling that there is a broad emission band whose total intensity is about $\frac{1}{4}$ of the total line intensity, we again find that $\frac{1}{10}$ of the emission is contained in the 5893.1-A line.

Threshold Conditions

It may be shown (see reference 2) that to initiate oscillation in an optical maser, we must have

$$N_2-N_1\geq\frac{4\pi^{\frac{3}{2}}}{(\ln 2)^{\frac{1}{2}}}\frac{g_1}{g_2}\frac{1}{\lambda^2}\Delta\nu\frac{(1-R)}{D}\tau_{21},$$

where N_2-N_1 is the population difference/cm^3 between the upper and lower states, R is the reflectivity of the mirrors at the ends of the rod, and D is the length of the rod in cm. The remaining symbols are as defined above. In the 5893.1A line $g_1=g_2=1$ and we will assume $R=0.8$, $D=1$ cm. We obtain $N_2-N_1\geq 2.3\times 10^{18}/\text{cm}^3$, where $\Delta\nu=1.5\times 10^{10}$ cps has been assumed.

This determines the europium concentration which we must put in our crystals. The most important criterion, however, is the pumping power required to initiate oscillations. The number of spontaneous decays into the 5893.1-A line at threshold would be N_2/τ_{21}. If η_{21} is the fraction of the absorbed quanta which are emitted as the 5893.1 A line, then the number of quanta which must be absorbed is

$$N_2/\eta_{21}\tau_{21},$$

and if the average size of the quanta used in pumping the fluorescence is $h\nu_p$, then the threshold power is

$$P_{\text{th}}=N_2 h\nu_p AD/\eta_{21}\tau_{21},$$

where AD is the volume of the oscillating material.

Assume that there are 2.5×10^{19} europium ions/cc in the crystal. At 20°K there would be only 10^9 of these ions/cc excited to the state at 307.4 cm^{-1} at thermal equilibrium. Setting $N_1=0$, $h\nu_p=4$ ev$=6.4\times 10^{-19}$ w-sec, $\eta_{21}=0.1$, $D=1$ cm, $\tau_{21}=0.08$ sec, and $A=0.1$ cm^2, we obtain $P_{\text{th}}=18.4$ w.

This value is sufficiently small that there is a reasonably high probability that stimulated emission can be observed at 5893.1 A in CdF_2:Eu, S. There remain, however, as yet unmeasured characteristics such as the optical homogeneity and the lifetime of the terminal state which may alter this conclusion.

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