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Aerospace Research Center

MATERIALS DEPARTMENT

LIQUID LASER PARAMETERS

Semi-Annual Technical Report
Contract NOnr 4644(CO)
1 August 1967 – 31 January 1968

Prepared for the
Scientific Officer
Physical Sciences Division
Office of Naval Research
Washington 25, D.C.

by

Dr. Norman Blumenthal
Dr. Cecil B. Ellis
Dr. David Williams
Dr. Daniel Grafstein

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GENERAL PRECISION SYSTEMS INC.
KEARFOTT GROUP
LITTLE FALLS, NEW JERSEY
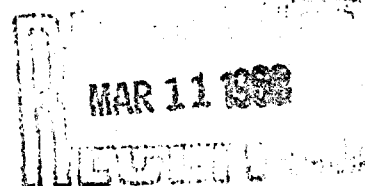
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Approved: _____

Dr. Daniel Grafstein
Principal Staff Scientist
Manager, Materials Department

General Precision Systems Inc.
Kearfott Group
Little Falls, New Jersey

FOREWORD

This is the Semiannual Technical Report on liquid laser parameters which covers research done under Contract NOnr 4644(00) between the Office of Naval Research and the General Precision Systems Inc., Aerospace Research Center, Little Falls, New Jersey. This report covers research performed during the period 1 August 1967 through 31 January 1968.

The work reported here was done by Dr. Norman Blumenthal and Dr. David Williams, assisted by Mr. Alfred Brauer, under the direction of Dr. Cecil Ellis and Dr. Daniel Grafstein, Manager of the Materials Department.   Dr. Irving Rowe of the Office of Naval Research, New York, has acted as Project Scientist.

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ABSTRACT

A number of techniques, such as elemental analysis, molecular weight determination, UV and IR absorption spectra, conductivity measurements and phosphorescence intensities were employed to determine the composition and structure of the europium, terbium and neodymium complexes of dimethylacetamide (DMAC) in both the solid state and in DMAC solutions. From the data obtained it was concluded that DMAC acts as a bidentate ligand; coordinating to the rare-earth ion through both oxygen and nitrogen. The empirical formula of the solid complexes is $M(DMAC)_3Cl_3$, where M equals the rare-earth ion. The solid DMAC complexes dissociate into two ionic species, $M(DMAC)_3Cl_2^+$ and Cl^-, when dissolved in DMAC.

Because the solubility of hydrated terbium salts in DMAC was found to far exceed that of the corresponding anhydrous salts, very concentrated solutions of $Tb(NO_3)_3 \cdot 6H_2O$ in DMAC could be prepared. Although water has a quenching effect on phosphorescence, the much larger number of terbium atoms per cc more than offsets this effect, so that the total solution phosphorescence intensity was enhanced some thirteen times over that for a saturated solution of anhydrous $TbCl_3$ in DMAC.

Neodymium phosphorescence (at 1.06μ) was found to be much more sensitive to quenching by liquids having high frequency C-H or O-H stretching vibrations than either terbium or europium. As a result neodymium phosphoresces only very weakly in DMAC. A new solvent was found in which neodymium phosphoresces almost a hundred times more intensely than in DMAC. This is the phosphorus oxychloride ($POCl_3$)-tin tetrachloride ($SnCl_4$) system in which neodymium oxide (Nd_2O_3) is quite soluble. This liquid has low viscosity at room temperature and appears to have good properties for use as a liquid laser. Preliminary but significant evidence for lasing in this Nd_2O_3-$POCl_3$-$SnCl_4$ system near 1.06μ is presented.

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I.   INTRODUCTION

The present work is a continued investigation of factors influencing the phosphorescence characteristics of Nd, Eu, and Tb trivalent compounds in liquid organic and inorganic solvents. This report covers the period 1 August 1967 through 31 January 1968.

Among the points which had been established previous to 1 August 1967 were the following, which may be understood by reference to Figure 1.

(a) If Eu-bearing liquids are excited by pumping into the high Eu^{3+} levels around 25,000 cm^{-1}, the Eu ions relax downward from these levels very quickly ($\sim 70 \mu$ sec) by non-radiative processes.

(b) Between 20% and 55% of the relaxing Eu ions, in the various pumped liquids investigated, probably initially relax down to the $^5D_0$ level at 17,000 cm^{-1}, (the largest such percentages occurring in liquids which have a P=O or C=O bond adjacent to the excited Eu). The remainder are relaxed quickly down to the ^7F multiplet by non-radiative processes.

(c) Of those Eu ions reaching $^5D_0$ the fraction which remains long enough to yield observable radiation varies enormously in different liquids. In water solutions of Eu salts there is hardly any phosphorescence at all. Apparently, multiples of the fundamental O-H vibration at ~ 3500 cm^{-1} take up the $^5D_0$ excitation energy immediately, in a further non-radiative relaxation to the ground multiplet.

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ENERGY LEVEL DIAGRAM FOR TRIVALENT RARE-EARTH IONS
FIGURE 1

(d) However, in some other liquids where the vibrational energy of the bond immediately adjacent to the excited Eu ion is much smaller than the $\leq 12,000$ cm^{-1} energy to be transferred, the tendency for non-radiative energy is much less, and the $^5D_0 \rightarrow {}^7F$ phosphorescence lines are much brighter, with correspondingly better prospects for lasing in one of these lines.

(e) The strongest phosphorescence occurs in liquids where the bond adjacent to the excited Eu is either P=O, with its fundamental vibration ~ 1200 cm^{-1}, or C=O, with its fundamental vibration ~ 1600 cm^{-1}.

(f) Results for Tb-bearing liquids are rather similar, with phosphorescence lifetimes for transitions down from the $^5D_4$ level being greatest when the bond adjacent to the Tb is P=O.

The bulk of the work for the period reported here falls into two most important classes. First, there were a number of attempts to define more closely the structure of the solvation sphere surrounding a rare-earth ion in one particular solvent, since the above work has emphasized the strong effect of the nearest neighbors on phosphorescence intensity. The solvent chosen was dimethylacetamide (DMAC), which shows the brightest phosphorescence observed from solvents with a C=O bond adjacent to the rare earth. The various lines of attack included elemental analysis of the crystals, vapor pressure and conductivity measurements on the liquids, studies on numerous homologues of DMAC, and mapping of UV and IR absorption spectra. The conclusion was reached that the rare earth ion is attached to the ligands by bidentate linkages involving both O and N

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atoms, and that two anions are produced when the solid complexes are dissolved in DMAC. Thus, the composition of the chlorides in DMAC solution is formulated as $M(DMAC)_3Cl_2 + Cl^-$.

A few measurements were also made on rare earth-DMAC-H_2O systems, which seem to have an even more complicated arrangement around the rare earth ion.

The second major class of work reported is the study of Nd spectra. Acquisition of new equipment has made possible some investigations of the 1μ spectra of Nd phosphorescence emission in several liquids. Since the level from which phosphorescence arises, $^4F_{3/2}$, is only 5500 cm^{-1} above the nearest ground multiplet level, non-radiative relaxation from $^4F_{3/2}$ is usually very probable. Thus, H_2O solutions of Nd salts hardly phosphoresce at all, and even the emission from the C=O compound, DMAC, was found to be much weaker than with Eu and Tb. However, a solvent in which the bond adjacent to the Nd is P=O has now been found which does indeed give strong 1μ Nd phosphorescence in the liquid state. This system is a mixture of $POCl_3$ and $SnCl_4$ which is able to dissolve Nd_2O_3. A brief description is included in an Appendix on the recently obtained evidence for Nd lasing in this liquid.

A final section of the report mentions some explorations on another class of solvents, fused halide and nitrate salts, where the environment of the rare earth ion is quite different from the cases studied so far.

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II.   NATURE OF THE RARE EARTH-DMAC SYSTEM

In order to understand exactly how the chemical environment of the rare earth ion affects the phosphorescence, it is critical to establish just what that environment is. This means a detailed analysis of the molecular composition and structure of the complex using the tools of elemental analysis, molecular weight determination, ultraviolet and infrared spectroscopy, and any other experimental technique which will assist in the study.

A.   Analysis of Anhydrous Crystalline Samples

A distillation train was set up which was continually purged with dry nitrogen, and the solvents distilled from various drying agents. An inert atmosphere box was procured for the actual sample preparation. Hydrated rare earth salts were dissolved in pure solvent and the excess solvent was then driven off under vacuum, leaving crystals of the rare-earth-ligand-solvent complex. This process was repeated leaving crystals analytically pure and virtually water-free. The samples were then sent to Galbraith Laboratories for compositional analysis.

The first samples of the corresponding Nd, Tb and Eu complex were prepared and analyzed, and the results are given in Table I. The theoretically calculated values are based on three dimethylacetamide ligands and three chloride ions. The analyses indicate that the molecular formulas for these complexes are thus: $Eu(DMAC)_3Cl_3$, $Tb(DMAC)_3Cl_3$, and $Nd(DMAC)_3Cl_3$.

TABLE I

Elemental Analyses of DMAC Complexes

		% C	% H	% N	% Cl
Eu(DMAC)$_3$Cl$_3$	Calc.:	27.8	5.21	8.11	20.5
	Found:	28.8	5.77	8.56	19.2
Tb(DMAC)$_3$Cl$_3$	Calc.:	27.4	5.13	7.99	20.3
	Found:	26.0	5.19	7.70	19.9
Nd(DMAC)$_3$Cl$_3$	Calc.:	28.2	5.27	8.21	20.8
	Found:	28.8	5.74	8.16	18.7

A molecular weight determination was also performed by Galbraith Laboratories on Eu-Cl-DMAC, and the result obtained was approximately half the theoretical molecular weight for $Eu(DMAC)_3Cl_3$. To perform the analysis, they dissolved the crystals in dimethylformamide (DMF) and measured the lowering of the vapor pressure, a phenomenon associated with the number of particles in solution.

Due to the great similarity of the chemistry of DMAC to DMF, no significant measured molecular weight difference is expected between these two solvents.

Since the observed molecular weight is one-half the formula weight, it is concluded that the molecule must dissociate into two particles. There is only one likely dissociation mechanism which yields two distinctly different molecular entities when one molecule of the rare-earth-DMAC complex is dissolved in DMAC. This is indicated by the following equation:

$$Eu(DMAC)_3Cl_3 \rightleftharpoons Eu(DMAC)_3Cl_2^+ + Cl^-$$
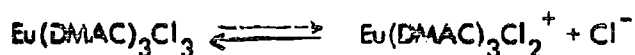
Further dissociation of the complex, in DMAC solution, would produce more Cl^- ions which would act as separate particles and produce an apparent molecular weight less than one-half the molecular formula.

B. Conductivity Measurements

A further check on the above molecular weight and dissociation considerations would be enhancement of the conductivity of pure DMAC when the complex is

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dissolved in it. The postulated dissociation mechanism in DMAC solution requires that almost all of the initially neutral complex molecules dissociate into two charged species.

To investigate this matter, a conductivity cell was obtained and a constant temperature bath set up. Measurements definitely indicated a large conductivity increase of the solution over that of pure DMAC, thereby proving that the neutral complex undergoes a significant dissociation into ionic species.

C. UV and IR Absorption Spectra

If one examines the UV and visible absorption spectra of these complexes dissolved in DMAC, run versus a pure DMAC blank, a strong UV absorption attributable only to the complex is present. This absorption is shifted some 400Å toward the visible from the usual UV absorption of pure DMAC, which indicates at least a partial delocalization of the DMAC carbonyl electrons.

Also, the IR absorption spectrum of the complex in solution shows a shoulder on the carbonyl-stretch band not present in the pure solvent. This can be attributed to a lowering of the carbonyl-stretch frequency within the complex by some 40 cm^{-1}. The conclusion is that the DMAC is coordinated to the rare-earth ion through the carbonyl oxygen.

D. General Conclusions on Studies

The results noted above would seem to indicate that in the crystalline form, the DMAC complexes are composed of three DMAC molecules and three

chloride ions for each rare earth ion, and in solution one of the chloride ions is free, leaving the ion $M(DMAC)_3Cl_2^+$.

On an investigation of certain homologs of dimethylacetamide, to be discussed in the next section, it was found that when a hydrogen atom is bonded to the nitrogen of the amide group, phosphorescence is severely quenched. This indicates that the nitrogen is also coordinated to the rare-earth ion, for only an N-H bond immediately adjacent to the rare-earth ion is considered to be capable of influencing the phosphorescence to such an extent. It was therefore concluded that DMAC is acting as a bidentate; that is, coordinating through both oxygen and nitrogen.
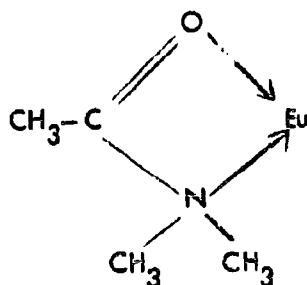
DMAC Coordinated to Europium

This result was not totally unexpected since coordination numbers of eight or nine (counting the chlorines) are fairly common for rare-earth ions.

As relates to the potential of developing a liquid laser, this fact that the ligand behaves as a bidentate has little effect. It does mean, however, that substituents which affect either the carbon-oxygen or the carbon-nitrogen bond may influence the rare-earth phosphorescence, and that the DMAC system is more complicated than was originally anticipated.

E. Phosphorescence in Homologs of Dimethylacetamide

A number of homologs of dimethylacetamide were investigated as ligands. The phosphorescence intensity of each complex with europium is noted in Table II for both the 619 mμ and 595 mμ line (which have different terminal levels, as shown by Figure 1), as well as the ratio of intensity of the 619 mμ line to the 595 mμ. All measurements were made on the hydrated salts dissolved in excess solvent.

Several things can be noted from Table II. For the first two complexes listed, the difference is not in the ligand but in the anion. The chloride complex has significantly weaker intensity than its nitrate analog. This type of behavior has been noted before (e.g., triethylphosphate complexes), and is proof that the anion plays a role in influencing the phosphorescence of the rare-earth ion. This again means that the anions are at least partially within the coordination sphere of the rare-earth ion in solution, and hence bonded to it. A nitrate ion has a vibration at 1380 cm^{-1} whereas, of course, a chloride ion has no internal molecular vibrations at all. Thus, it appears that the nitrate vibration is enhancing the phosphorescence, and, consistent with our hypothesis put forth in the last semiannual (1 February 1967 - 31 July 1967), may be assisting the nonradiative transitions _to_ the emitting level to a greater extent than _from_ the emitting level.
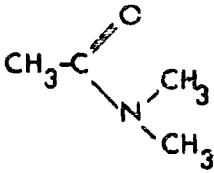
TABLE II

Phosphorescence Intensities of DMAC Homologs

Complex	Ligand	Intensity 619 mμ	Intensity 595 mμ	I_{619}/I_{595}
Eu-N-Dimethylacetamide	$CH_3-C\overset{O}{\underset{N}{<}}\overset{CH_3}{\underset{CH_3}{}}$	104	20.3	5.14
Eu-Cl-Dimethylacetamide		40.6	12.2	3.33
Eu-N-Dimethylformamide	$H-C\overset{O}{\underset{N}{<}}\overset{CH_3}{\underset{CH_3}{}}$	82.5	18.9	4.36
Eu-N-Diethylformamide	$H-C\overset{O}{\underset{N}{<}}\overset{C_2H_5}{\underset{C_2H_5}{}}$	88.1	18.3	4.81
Eu-N-Dibutylformamide	$H-C\overset{O}{\underset{N}{<}}\overset{C_4H_9}{\underset{C_4H_9}{}}$	77.3	14.8	5.22

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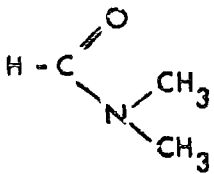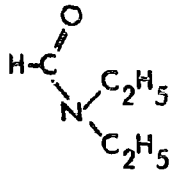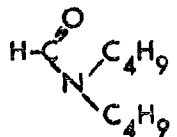
TABLE II (Continued)

Complex	Ligand	Intensity		I_{619}/I_{595}
		619 mμ	595 mμ	
Eu-N-Dimethylpropionamide	CH_3-CH_2-C O / N CH_3 / CH_3	94.0	14.3	6.56
Eu-N-Dimethylacrylamide	$CH_2=CH-C$ O / N CH_3 / CH_3	Insoluble		
Eu-Cl-Ethylacetamide	CH_3-C O / N H / C_2H_5	9.16	3.05	3.01
Eu-Cl-Methylacetamide	CH_3-C O / N H / CH_3	3.19	1.10	2.90
Eu-Cl-Methylformamide	$H-C$ O / N H / CH_3	<1.0	<1.0	--
Eu-N-Diisopropylacetamide	CH_3-C O / N $CH(CH_3)_2$ / $CH(CH_3)_2$	Insoluble		

Looking further at the table, there is definite evidence that complexes with monosubstituted amide ligands, that is, those with a hydrogen atom on the nitrogen, yield far weaker phosphorescence than complexes having di-substituted ligands. This is consistent with the idea that a hydrogen bond adjacent to the metal ion provides an excellent mechanism for quenching phosphorescence. If we compare the nitrates of dimethylacetamide and dimethylformamide, we note that the hydrogen on the carbon seems to quench the phosphorescence more than a methyl group, but nowhere as much as a hydrogen on nitrogen. It should be noted, however, that the numbers given are probably good to only 5 percent, and small differences should not be considered significant.

One puzzling aspect is the insolubility of the dimethylacrylamide complex when compared with the dimethylpropionamide complex. The presence of a double bond should not drastically affect solubility. One possible explanation is the tendency for this type of molecule to polymerize, which would limit its solvent properties, although we have no evidence that polymeriza-tion has occurred .

From the above investigation of DMAC homologues, one can see that mole-cular changes consisting of adding on varying numbers of $-CH_2-$ groups to the DMAC molecule result in only negligible alterations in phosphorescence proportios. Therefore, no further work in this direction seems necessary.

III. MEASUREMENTS ON THE RARE EARTH-DMAC-H_2O SYSTEM

A. Enhancement of Tb Phosphorescence

An experiment was performed to examine the relative solubilities of anhydrous and hydrated rare-earth salts in DMAC. It was found that the solubility in DMAC of hydrated salts (salts containing water of crystallization) far exceeds that of the corresponding anhydrous salts. This is presumably because at least one water molecule remains solvated to the rare-earth ion in the organic liquid, thereby creating an environment more closely approximating that of an aqueous solution in which the salts display great solubility.

As is already well known, water has a strong quenching effect on rare-earth phosphorescence, so that one might suppose that any DMAC solution of a hydrated salt would display a weak output. However, it was found that the actual phosphorescence intensity of a 0.44 M solution of $Tb(NO_3)_3 \cdot 6H_2O$ in DMAC is about thirteen times brighter than a saturated anhydrous $TbCl_3$-DMAC solution (Table III) which is approximately .02 M.

The above figures show that intensity per terbium atom in the solution of the hydrated salt is only about 60 percent of that in the anhydrous system. However this intensity decrease per atom is more than offset by the much larger number of terbium atoms per cc, so that the total phosphorescence intensity from the solution is greatly enhanced. An interesting conclusion to be drawn from these observations is that the presence of approximately one water molecule per solvation sphere around the Tb causes for less quenching than the case of a complete H_2O solvation sphere which obtains in water solutions of Tb salts.

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TABLE III

Relative Phosphorescence Intensities of Neodymium and Terbium in Different Solvents

Concentration	Liquid	Relative Intensities[1]	
~ 0.02 M(Sat)	$TbCl_3$-DMAC Anhydrous	5 (5477Å)	5 (4875Å)
0.44 M (~ Sat)	$Tb(NO_3)_3 \cdot 6H_2O$-DMAC	65 (5433Å)	65 (4888Å)
~ 0.1 M	Nd_2O_3-$POCl_3$-$SnCl_4$	85 (1.06μ)	
0.10 M (~ Sat)	$NdCl_3$-DMAC Anhydrous	1.0 (1.06μ)	
1.0 M	$Nd(NO_3)_3 \cdot 6H_2O$-DMAC	Undetectable (1.06μ)	

(1) All intensities have been corrected for the known response characteristics of the 7102 photomultiplier and the xenon excitation lamp.

Further experiments showed that dilution of the 0.44 M solution with DMAC resulted in a phosphorescence intensity decrease which was directly proportional to the dilution factor. This constancy of emission intensity per Tb ion indicates that no significant self-quenching of the terbium (through Tb-Tb interactions) had been occurring in the concentrated solution, provided one may assume an unvarying constitution of the solvation sphere as more DMAC is added. Evidence for the latter point is the lack of change in the structure of the spectrum accompanying this dilution.

B.   Fine Structure Variations in Tb and Eu

Another technique, aside from conductivity measurements for establishing the existence of more than one molecular species in solution is the study of the splitting of the phosphorescence bands into a multiplet structure; each component arising from some particular entity. The Aminco-Bowman spectrophotofluorimeter, previously employed for phosphorescence work, has a low resolution capability; certainly too low to have resolved the spectral differences between the tris and tetrakis   europium chelates. To improve this situation, a Jarrell-Ash 0.5 meter Ebert scanning monochromator was set up in conjunction with a 150 watt xenon excitation lamp and an 1P21 photomultiplier tube feeding a recorder through an amplifier. Suitable filtering of the exciting light was used in order to completely remove the europium and terbium phosphorescence wavelength regions, so as to minimize any interference. Another filter removed the infra-red to prevent the heating of the sample. This monochromator has a dispersion of 16A per mm and was used with a 30 μ output slit giving an actual resolution capability of 0.48A.

With this experimental set-up, solutions of anhydrous and hydrated europium and terbium salts in DMAC were examined for resolvable fine structure in their phosphorescence spectra. A saturated anhydrous $TbCl_3$ solution in DMAC yielded spectra where the $^5D_4 \rightarrow {}^7F_6$ (approximately 490 mu) phosphorescence transitions were split into doublets (Table IV).

In an attempt to establish the origin of these doublets, two drops of water were added to 3 cc of the anhydrous solution. This resulted in the disappearance of one of the components from each of the doublets, and a considerable overall decrease in the phosphorescence intensity from both of the transitions.. The frequency of the remaining lines are very close to those from both an aqueous solution of $TbCl_3$ and a DMAC solution of $Tb(NO_3)_3 \cdot 6H_2O$.

Due to the complexity of the systems it is not possible to determine unambiguously what molecular changes are responsible for the above result, although two explanations come to mind as being reasonable. The supposed anhydrous solution may not be strictly dry and may contain a small amount of water. If there was not enough water to contribute at least one molecule to the first solvation sphere of all the terbium ions, then two molecular species would exist; some possessing at least one water about the terbium and others none. The two species would then have different rare-earth environments and could give rise to phosphorescence spectra at somewhat different frequencies. Adding more water would assure that all of the terbium ions have at least one water in close proximity and the spectra from the species with no water would, of course, disappear. The decreased phosphorescence intensity would then result from the well known quenching effect of water.

TABLE IV

Phosphorescence Wavelengths of Europium and Terbium in DMAC and Water Systems

	Wavelength in Å of Center of Phosphorescence Peaks
$Tb(NO_3)_3 \cdot 6H_2O$ -DMAC	5433
	4888
$TbCl_3$ -H_2O	5430
	4884
$TbCl_3$ -DMAC Anhydrous	5477 } 5423 }
	4952 } 4875 }
$TbCl_3$ - DMAC Anhydrous plus small amount of water	5435
	4878
$EuCl_3$ -DMAC Anhydrous	6115
	5910
$EuCl_3$ -DMAC Anhydrous plus small amount of water	6115
	5910
$EuCl_3$ -H_2O	6119
	5910
$Eu(NO_3)_3 \cdot 6H_2O$ -DMAC	6166
	5985

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Alternatively, the anhydrous system may be strictly dry and the splitting may result from the lifting of the degeneracies of the emitting and terminal levels by a strong electric field of a particular symmetry resulting from the coordination sphere around the terbium. The addition of water can now create an environment of different symmetry which does not split the degenerate terbium levels into as many components as before, so that only one band is observed.

As can be seen from Table IV the europium nitrate and chloride-DMAC and water solutions do not display any splitting of the phosphorescence bands, although a close examination of the band shape reveals some asymmetry which is indicative of the possible presence of unresolved overlapping components. It is not yet clear why the europium and terbium systems behave in such a different manner. However, the Eu levels have smaller J-values than the Tb levels, and so might display a lesser spread of local field components.

IV. Nd SOLUTION SPECTRA

A. Neodymium Phosphorescence Detector Assembly

Near the end of the period covered by this report a complete infra-red detector assembly was received from American Instrument Company. This consists of a 7102 photomultiplier tube, cooling dewar, power supply, and solid state amplifier. With the multiplier cooled to dry ice temperature the residual dark current becomes almost negligible and we are able to accurately measure even very weak signals at the 1.06μ neodymium phosphorescence line. At present this detector assembly is being used on the Aminco-Bowman spectrophotofluorimeter with an infra-red grating, but it can be readily attached to any monochromator. Now that we were able to readily study the 1.06μ neodymium phosphorescence spectra, an intensive examination of a great variety of neodymium-containing liquid systems was begun. This program should bring our understanding of neodymium systems to at least the same level as that of europium and terbium.

B. Neodymium-DMAC Studies

A 0.1 M solution (practically saturated) of anhydrous $NdCl_3$ in DMAC displayed a weak phosphorescence at 1.06μ as compared with the intensity in the green from the corresponding anhydrous terbium system. From Table III we see that per neodymium atom the intensity is approximately .04 times that of the per-atom terbium intensity.

Although the Nd salt containing water of crystallization, $Nd(NO_3)_3 \cdot 6H_2O$, was soluble to the extent of 1.0 M in DMAC, no 1.06μ phosphorescence could be detected at all, in strong contrast to the situation for the Tb case.

This indicates the extreme sensitivity of neodymium phosphorescence to the proximity of water molecules to the neodymium atom, since at least one water molecule is present in the immediate solvation sphere of the rare-earth.

In the light of our ideas which view non-radiative transitions as arising from transfer of the electronic energy of the rare-earth atom to vibrational modes of groups in close proximity, we can rationalize the above difference between Nd and Tb behavior. The efficiency of energy transfer progressively falls as the bond which is being vibrationally excited is moved further from the rare-earth. Also, if one has to excite a high vibrational overtone to accept the energy then the transfer is very much less efficient than if the transfer can be accomplished by excitation of a low overtone. Since the energy gap in Nd between the emitting level $(^4F_{3/2})$ and the next lowest level $(^4I_{15/2})$ is only 5500 cm^{-1}, one can readily see that for C-H and O-H stretching vibrations, which are usually broad bonds from 3000 to 3500 cm^{-1}, a vibrational excitation to the second overtone (v = 2 level) will suffice. In terbium the similar energy gap is approximately three times as many wavenumbers so that non-radiative energy transfer, which must now involve high frequency vibrations, is very much less efficient.

Thus, even though the C-H stretching vibration present in DMAC is removed from the immediate vicinity of the neodymium (which is coordinated through the oxygen and nitrogen), it is still very effective in promoting non-radiative relaxations among the closely spaced energy levels of that ion. It appears, therefore, that in order to obtain really strong 1.06μ neodymium phosphorescence, one would have to completely remove all high frequency vibrations from the solvation sphere of the ion.

C. Neodymium in $POCl_3$-$SnCl_4$

To accomplish the above mentioned aim, we have now found an inorganic system in which neodymium does display a very intense 1.06 μ phosphorescence. This is a mixture of $POCl_3$ (phosphorus oxychloride) and $SnCl_4$ (stannic chloride). The highest vibration in this system is the P=O stretch at 1285 cm^{-1}. From Table IV one can see that the 1.06 μ neodymium phosphorescence in this system (~0.1 M) is approximately three times greater than for $TbCl_3$-anhydrous-DMAC on a per-atom basis, and about eighty-five times greater than an anhydrous $NdCl_3$-DMAC solution of equivalent concentration.

The system being studied here is similar in many respects to the $Nd:SeOCl_2$ laser previously described [1,2]. In that system tin tetrachloride was added to selenium oxychloride in order to dissolve the otherwise poorly soluble neodymium oxide.

The chemistry of phosphorus oxychloride and its adducts with various aprotic acids, including tin tetrachloride, has been studied [3,4]. With tin tetrachloride in phosphorus oxychloride the species $POCl_2^+$ and $SnCl_6^=$ are presumed to be generated which, in turn, act to dissolve the neodymium oxide.

Solutions were easily prepared by adding neodymium oxide to the mixed solvent (5 volumes of $POCl_3$ to 1 volume of $SnCl_4$), heating to incipient boiling, cooling and centrifuging to remove any suspended matter. No special handling precautions are required except for the gloves and fume hood normally employed with reactive acid chlorides. The system has the advantages of low toxicity, and high mobility at room temperature. The

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5:1 proportion of $POCl_3$ to $SnCl_4$ insures that the system remains liquid at room temperature. Higher proportions of tin tetrachloride generate solid adducts at room temperature.

This and related systems will be studied further during the next period.

V.   FUSED SALT SYSTEMS

In a separate but related study in this laboratory we have begun an examination of the possibility of using fused salt systems as liquid media for rare-earth ions. There is very little information in the literature concerning phosphorescence of rare-earth ions in fused salts and it would seem to be an area for fruitful investigation.

In our studies, an upper limit of about $200^\circ C$ has been set on the melting point of any salt or salt mixture to be investigated, partly because of experimental convenience and partly because it is well known that phosphorescence is quenched at not too elevated temperatures. Also, only those systems that are optically clear from $0.5\,\mu$ to $1.1\,\mu$ in the liquid state are being considered.

The initial phase of this study consisted of an examination of the solubility and phosphores- cence properties of anhydrous europium (III), terbium(III), and neodymium(III) chlorides and oxides in various low-melting salt mixtures. Thus far, we have made two preliminary and very interesting observations concerning the solubility and phosphorescence of terbium(III) and europium(III) chlorides in a potassium nitrate - lithium nitrate eutectic which melts at $139^\circ C$. In this eutectic at about $150^\circ C$, $EuCl_3$ is very soluble, at least to the extent of 1 M, and the resulting solution displays a very intense phosphorescence when excited by a UV lamp. In this same eutectic $TbCl_3$ displays a similar solubility but its phosphorescence is completely quenched. In order to obtain quantitative information about these systems, it will be necessary to modify our phosphorescence-measuring apparatus to be used at elevated temperatures.

VI.   FUTURE PLANS

The research in the next period will concentrate on neodymium phosphorescence in order to bring our understanding and knowledge in this area to the level of that for europium and terbium systems.

1. An intensive study will be carried out on systems containing neodymium compounds dissolved in $POCl_3$, $PSCl_3$, related heavy metal halides and oxyhalides, and mixtures of the above.

2. The effect on neodymium phosphorescence of replacing hydrogens and hydroxyl (OH) groups in organic molecules by halogens in certain organic solvents, will be studied. This eliminates the high frequency CH and OH stretching vibrations.

VII. REFERENCES

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APPENDIX

Evidence for Lasing of Nd_2O_3-$POCl_3$-$SnCl_4$

Shortly after the close of this report period, strong emission with a "spiking" action very similar to that in a ruby laser was observed with a dilute solution of Nd_2O_3 in a 5:1 mixture of $POCl_3$ and $SnCl_4$ upon excitation with the 5000 joule pulse of a helical xenon flash lamp. The IR output was detected through a 1.06 μ interference filter with a 925 photodiode feeding a 545 Tektronix scope across a 47 ohm load resistor. The liquid was contained in a 12mm i.d., 12.5 cm long tubular quartz cell. Quartz optical flats were cemented to the ends with epoxy. External plane mirrors with dielectric coatings were aligned parallel to the ends of the cell. One mirror had more than 99 percent reflectivity and the other had 10 percent transmission at 1.06 μ.

Figure 2 shows the smooth fluorescence decay curve below threshold. Above threshold in Figure 3 one sees a burst of spiking of very much greater intensity than the background neodymium fluorescence and pump light. Figure 4 shows the first section of the random spiking pattern on an expanded time scale.

Several improvements in the experimental arrangements are possible which can be expected to lower the threshold for lasing. Experiments are now proceeding with this system.
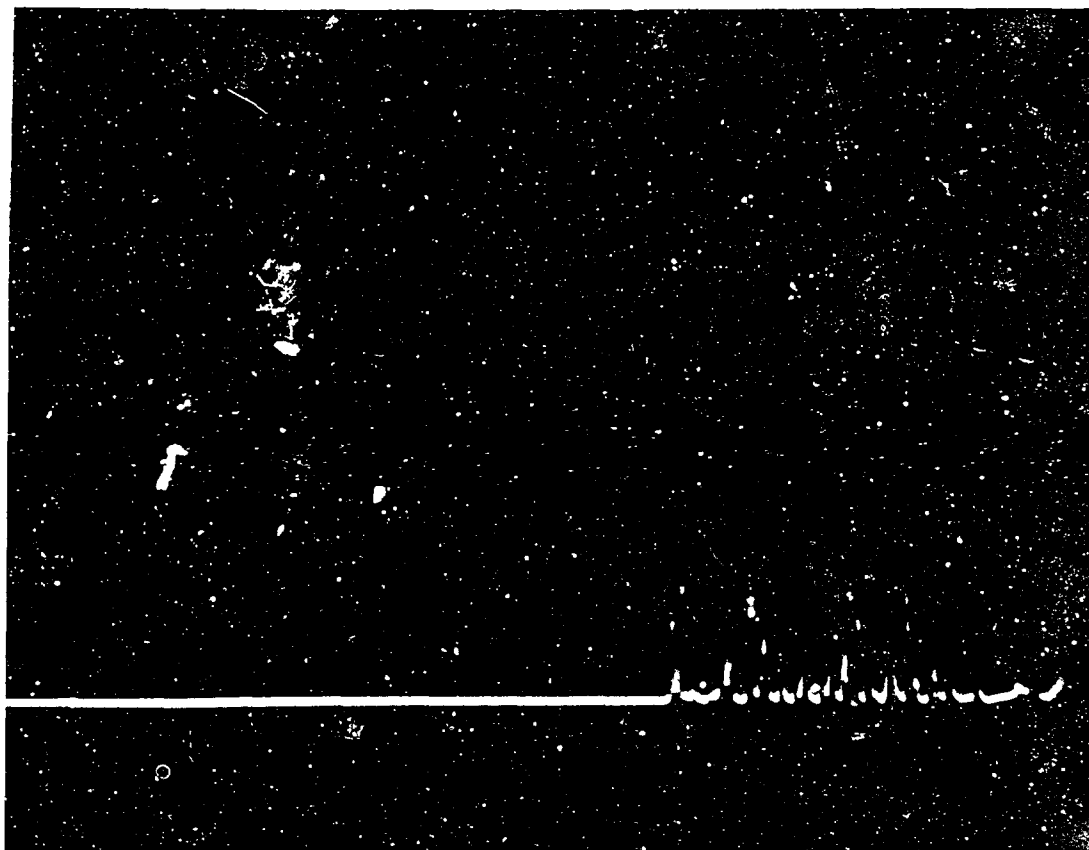
3300 JOULES INPUT

SMOOTH FLUORESCENCE DECAY BELOW THRESHOLD

100 MICROSECONDS/CM

FIGURE 2
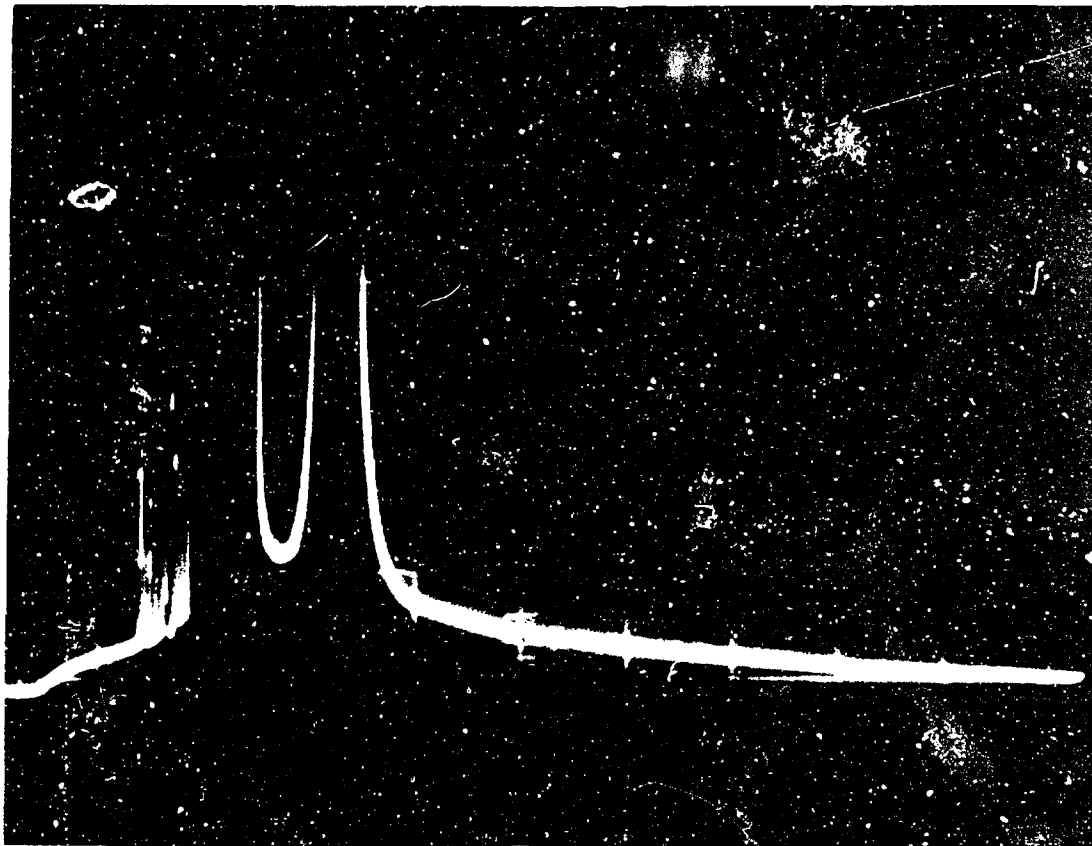
5000 JOULES INPUT
RANDOM SPIKING ABOVE THRESHOLD
100 MICROSECONDS/CM
FIGURE 3

5000 JOULES INPUT
FIRST PART OF SPIKING AS IN FIGURE 3 ON EXPANDED TIME
SCALE OF 20 MICROSECONDS/CM

FIGURE 4