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(5) 751 500
RCA Labs. Div.,
Radio Corp. of America,
Princeton, N.J.

(11) 15 April ~~15, 19~~64,

(OPTICAL CASE) (10)

(6) CaF_2 Laser Crystal Growth .
(16) Order ~~No.~~ 306-62
~~Contractor: RCA Laboratories~~
~~Contract Date: 4-1-63~~
~~Project Code No. 3730~~
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H. A. Weakliem, ~~WA-4-2700~~ X 2447
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Crystals of CdF_2 containing all of the rare earth ions have now been grown. As mentioned previously, the oxidation state is +3 in all cases and all attempts to reduce the rare earth to the +2 state have failed. A crystal of CdF_2:Tm^{+3} was heated to 750° C in an atmosphere of about 40 mm pressure of Cd for 15 minutes. The originally colorless crystal was blue after heating and the absorption spectrum showed that there was no decrease in the lines due to Tm^{+3} absorptions. There was a new absorption which increased with increasing wavelength. The absorption constant was found to be proportional to $\lambda^{3.5}$. This behavior is exactly that found for CdF_2:Sm^{+3} and reported by J. S. Prener and J. D. Kingsley, J. Chem. Phys. 38, 667 (1963). It therefore appears likely that all the rare earth doped CdF_2 crystals will show this behavior, giving a "free electron impurity band", and it is unlikely that one will be able to reduce rare earths in this host. We did not measure the conductivity of the crystals but expect that they are highly conducting.

A good crystal of CdF_2:Ni^{+2} has been grown and the absorption spectrum is superficially similar to that seen for ZnO:Ni. The double peaked strong absorption in the visible, typical of Ni^{+2} in tetrahedral sites, is centered about 5000Å (25,000 cm^{-1}) in CdF_2. It is difficult to account for this band lying some 10,000 cm^{-1} higher energy in CdF_2 than in ZnO simply on the basis of a higher electron exchange parameter, B, in the fluoride host compared to the oxide host. In fact, save for the fact that the band has two maxima, the spectrum can be explained better if it is assumed that Ni^{+2} is in an octahedral site, not a hexahedral one. There are, however, no such sites in CdF_2. The interstitial site has a

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hexahedral array of fluorides around it and an octahedral array of cadmium ions. However, the effective charges of the latter is expected to be small and positive, thus giving rise to the same energy level diagram as for the hexahedral array.

We have grown a single crystal of $CdCl_2$ containing Ni^{+2} in order to examine the spectrum of octahedrally coordinated Ni^{+2} in a lattice having no water molecules (whose vibrations obscure many features). We find a strong band at 21,300 cm^{-1} and weaker ones at 11,000 cm^{-1} and 6670 cm^{-1}. Dq is about 650 cm^{-1} and there seems to be no doubt that Ni^{+2} is in an octahedral site having a center of symmetry. At low temperatures there is a sharp line on the low energy side of the 6670 cm^{-1} band, lying at 5210 cm^{-1}. This is probably a magnetic dipole transition $^4A_2 \rightarrow {}^4T_2$. The transition is magnetic dipole allowed and is from the ground state to the first excited state. We also find a weak emission in this region of the spectrum.

The only emission seen for transition ions in CaF_2 or CdF_2 is for the ions Cr^{+3} and Mn^{+2}. The absorption spectrum of CaF_2:V strongly suggested emission near 1.1μ, however we have been unable to observe any emission from these crystals.

During this quarter our efforts to measure the width of the very narrow low temperature fluorescent lines of the $CaF_2:Tm^{2+}$ and $CaF_2:Dy^{2+}$ systems have continued.

The Fabry-Perot interferometer was aligned and focused using the 1.15μ radiation from a He-Ne gas laser. The resolution in this range was sufficient to easily resolve the longitudinal modes, separated by .004 cm^{-1}. Several exposures of several hours each at different interferometer mirror spacings (i.e. different resolutions) failed to show any sign of fringes due to the $CaF_2:Tm^{2+}$ 1.116μ fluorescence. Thus we have been unable to confirm our early tentative line width measurement of .01 cm^{-1} at 4.2°K. It appears that there is insufficient fluorescent intensity to expose the very low sensitivity photographic plates available for these wavelengths in a reasonable time. This approach has therefore been abandoned.

In the last quarterly report an optical magnetic resonance absorption technique for line width measurement was described. This technique has been applied to the fluorescent lines of both the Tm^{2+} and Dy^{2+} systems at 77° K and 27° K. The data are complicated by the presence of four Zeeman components in the Tm^{2+} case and three in the Dy^{2+} case, and by polarization effects. In order to understand these effects, line widths measured at 77° K are being compared with those measured by standard spectroscopic techniques. Corrections are also required for the temperature dependent line shifts such as those given in the previous report for two $CaF_2:Dy^{2+}$ lines.

We have also used standard high resolution spectroscopic methods to study the temperature dependence of the widths and wavelengths of these same fluorescent lines in the higher temperature range where they are broader. The $CaF_2:Tm^{2+}$ system was studied between 27° K and 373° K; the $CaF_2:Dy^{2+}$ system between 27° K and 195° K*. This data is being reduced and analyzed and will be included in the final report.

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*The work on the CaF_2Dy^{2+} system, which is of interest for laser applications, was also partially supported by the Air Force Avionics Laboratory, Research and Technology Div., Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, under Contract No. Af33(615)-1096. The work will be reported in both contracts.