

## Temperature Dependence of Edge Emission in Single-Crystal Cadmium Sulfide

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The temperature dependence of the two series of edge emission lines in single-crystal CdS has been studied in the range of 4.2 to 350°K. The "blue" or short-wavelength lines persist to 350°K, and at least three bands are directly associated with the low-temperature lines. The shortest wavelength band has a peak at 5092 Å at 300°K and is associated with line  $B_1$ <sup>1</sup> of Pedrotti and Reynolds which appears at 4853 Å at 4.2°K. The slope of the curve of wavelength versus temperature of this line is quite linear in the temperature range 175 to 350°K with slope of  $6 \times 10^{-4}$  eV/°K. At lower temperatures the slope becomes less and in the range 4.2 to 100°K is  $2 \times 10^{-4}$  eV/°K. In the case of the green fluorescence, under stimulation by 250-keV electrons at a current of  $5 \mu\text{A}/\text{cm}^2$ , there is a band with a peak intensity at 5490 Å at 300°K. At 77°K the peak intensity of this band is at 5250 Å. The intensity of the band is three orders of magnitude less at 300°K than at 77°K.

### INTRODUCTION

THERE have been several fluorescence bands observed in CdS near the band edge at room temperature.<sup>1-5</sup> Some of these have been claimed to be band-to-band recombination. The fluorescence near the band edge at low temperature has received much more attention and is understood in much greater detail.<sup>6-10</sup> We have studied the temperature dependence of the wavelength of edge emission in CdS between 4.2 and 350°K to identify the bands observed at room temperature with the bands observed at 77 and 4.2°K.

The "blue" and "green" bands are defined as according to Pedrotti and Reynolds.<sup>9</sup>

### EQUIPMENT AND TECHNIQUE

The crystals were single crystals of pure CdS grown by vapor phase deposition. They were mounted with rubber cement on a cold finger either beneath a nitrogen Dewar or a helium Dewar. The "blue" fluorescence was excited with a 500-W mercury lamp with appropriate filters. The "green" fluorescence at nitrogen temperature and above was excited with 250-keV electrons with an intensity of  $5 \mu\text{A}/\text{cm}^2$ . The fluorescence was measured with a Bausch and Lomb grating spectrometer with type 103aF plates or with a Perkin-Elmer glass prism spectrometer with a type-6199 phototube, as appropriate to the particular experiment.

### DATA AND RESULTS

Figure 1 shows the temperature dependence of the edge emission of three crystals. Two of these show only the blue emission bands at high temperature, one shows only the green. Crystal A had a large number of both green and blue lines at temperatures below 77°K, but above this temperature only the two very prominent blue lines persisted. At the higher temperatures the two fluorescence bands appear at different parts of the crystal. Crystal B, on the other hand, showed only three intense bands at 4.2°K. The longer wavelength fluorescence bands appeared as the temperature increased to 77°K, one splitting off from the other, as shown. Crystal C was of the type which shows mechanical stimulation of edge emission and at 4.2°K showed the second phonon peak to be the most intense, in agreement with Litton and Reynolds.<sup>10</sup> At 77°K the edge emission could not be resolved into bands, but the peak intensity occurred at the wavelength corresponding to the second phonon peak in crystals where the phonon structure of the green edge emission is resolved.

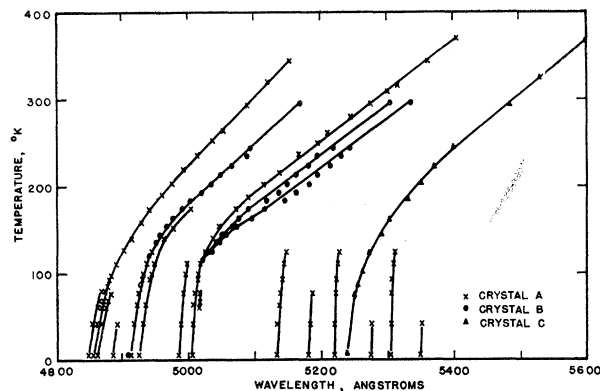


FIG. 1. Temperature dependence of edge emission in CdS.

<sup>1</sup> J. Fassbender, *Naturwiss.* **34**, 212 (1947).

<sup>2</sup> A. A. Vuylsteke and Y. T. Sihvonen, *Phys. Rev.* **113**, 40 (1959).

<sup>3</sup> Y. T. Sihvonen, D. R. Boyd, and C. D. Woelke, *Phys. Rev.* **113**, 965 (1959).

<sup>4</sup> C. E. Bleil and D. D. Snyder, *J. Appl. Phys.* **30**, 1699 (1959).

<sup>5</sup> M. Balkanski and F. Gans, *International Conference on Luminescence*, New York University, 1961 (unpublished).

<sup>6</sup> F. A. Kroger, *Physica* **7**, 1 (1940).

<sup>7</sup> C. C. Klick, *J. Opt. Soc. Am.* **41**, 816 (1957).

<sup>8</sup> D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **116**, 573 (1959); **122**, 25 (1961); **128**, 2135 (1962).

<sup>9</sup> L. S. Pedrotti and D. C. Reynolds, *Phys. Rev.* **120**, 1664 (1960).

<sup>10</sup> C. W. Litton and D. C. Reynolds, *Phys. Rev.* **125**, 516 (1962).

The intensity of the blue fluorescence crystals as a function of temperature was not quantitatively consistent from one crystal to another, but generally the intensity decreased by a factor of 10 from 4.2 to 77°K and by another factor of 10 between 77 and 300°K. The green fluorescence was, however, more consistent and under constant irradiation by 250-keV electrons at an intensity of  $5 \mu\text{A}/\text{cm}^2$ . The intensity as a function of temperature is shown in Fig. 2. It should be noted, however, that at 77°K the intensity was independent of the electron current density, while at 300°K the intensity of fluorescence varied linearly with electron beam current in the range 1 to  $10 \mu\text{A}/\text{cm}^2$ . The dashed curve is the data of Reynolds<sup>11</sup> for intensity of edge emission under ultraviolet irradiation.

The bands become wider as the temperature is increased. The blue bands at 4.2°K are about 10 Å wide, at 77°K the width increases to 35 Å, and at 300°K the width is of order of 70 Å. The green fluorescence bands at 4.2°K are 60 Å wide and are unresolvable at 77°K, but the total width at the half-intensity points is 250 Å. At 300°K the width has increased to 285 Å.

#### DISCUSSION

The knees in the curves in Fig. 1 show the necessity for a rather complete observation of the temperature dependence before conclusions are reached as to the temperature coefficients of this absorption edge. The slope of the line  $B_1$  in the high-temperature region is  $6 \times 10^{-4} \text{ eV}/^\circ\text{K}$ , and agrees closely with the slope of the absorption edge data of Dutton<sup>12</sup> at low absorption. At low temperatures, 4.2 to 75°K, the slope is  $2 \times 10^{-4} \text{ eV}/^\circ\text{K}$ . Over the entire temperature range the tem-

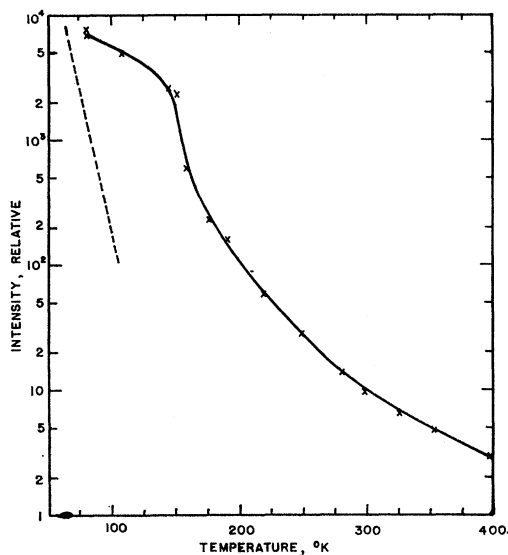


FIG. 2. Intensity of green edge emission as a function of temperature.

<sup>11</sup> D. C. Reynolds, Phys. Rev. **118**, 478 (1960).

<sup>12</sup> D. Dutton, Phys. Rev. **112**, 785 (1958).

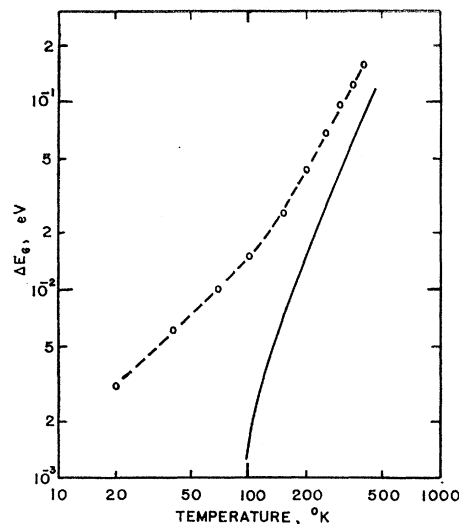


FIG. 3. Shift in band gap in CdS as a function of temperature. Solid line, theory of Fan and Radkowsky. Dashed line, experimental data.

perature dependence presented here agrees well with the temperature dependence of the absorption edge of Radelt.<sup>13</sup>

The data clearly show that the peaks at 300°K at 5100, 5175, and 5280 Å are associated with the low-temperature peaks at 4853, 4913, and 5002 Å. These have been identified as  $B_1$ ,  $B_2$ , and  $B_3$ , respectively, by Pedrotti and Reynolds. The band at 5490 Å at 300°K is associated directly with the series  $G_4$ ,  $G_6$ ,  $G_8$ , and  $G_{10}$  at 77 and 4.2°K. This series is commonly called the green edge emission at 77°K.

The shift in the absorption edge in semiconductors takes place as a result of lattice dilatation and electron-phonon coupling and possibly other effects. The effect of lattice dilatation can be determined if the pressure dependence of the band edge is known as well as the compressibility and temperature coefficient of expansion. In the high-temperature region Hohler<sup>14</sup> has measured the pressure dependence of the absorption edge. At low temperature Langer<sup>15</sup> has measured the pressure shift of the short wavelength fluorescence lines of CdS. Their results are in agreement. Thus, the energy of the first blue fluorescence line is closely associated with the band gap in CdS. Seiwert<sup>16</sup> has already shown that, from the absorption data, about one-sixth of the shift in the band gap with temperature is associated with lattice dilatation.

Radkowsky<sup>17</sup> and later Fan<sup>18</sup> have derived expressions for the shift in the band gap due to electron-phonon coupling. At temperatures where  $\hbar\omega/kT$  is of

<sup>13</sup> H. Radelt, Z. Naturforsch. **15a**, 260 (1960).

<sup>14</sup> G. Hohler, Ann. Physik **6**, 371 (1949).

<sup>15</sup> D. W. Langer and W. R. Lauterbach, Bull. Am. Phys. Soc. **6**, 111 (1961).

<sup>16</sup> R. Seiwert, Ann. Physik **6**, 241 (1949).

<sup>17</sup> A. Radkowsky, Phys. Rev. **73**, 749 (1948).

<sup>18</sup> H. Y. Fan, Phys. Rev. **82**, 900 (1951).

the order of one their expression may be written

$$\Delta E_g = \frac{-\pi(e^*e)^2}{\Omega M \omega^{3/2}} \left[ \left( \frac{2m_e^*}{\hbar^2} \right)^{1/2} + \left( \frac{2m_h^*}{\hbar^2} \right)^{1/2} \right] (n+1),$$

where  $n=1/[(\exp \hbar\omega/kT)-1]$ ,  $\omega$  is the angular frequency of the longitudinal optical phonon,  $\Omega$  is the volume of the unit cell,  $M$  is the reduced mass of the atoms,  $e^*$  is the effective ionic charge, and  $m_e^*$  and  $m_h^*$  are the effective masses of the charge carriers in the conduction and valence bands, respectively. For CdS,  $\omega=0.58 \times 10^{14}$ ,<sup>19</sup>  $e^*=0.72$ ,<sup>20</sup>  $m_e^*=0.7 m_e$ , and  $m_h^*=0.2 m_e$  and  $5.0 m_e$ ,<sup>8</sup> parallel and perpendicular to the  $c$  axis, respectively. Using these values the solid curve in

<sup>19</sup> R. J. Collins, J. Appl. Phys. **30**, 1135 (1959).

<sup>20</sup> F. Kefer, J. Chem. Phys. **33**, 1267 (1960).

Fig. 3 is plotted. The experimental data are plotted as the circles. While at high temperatures the theoretical curve is somewhat in agreement with the experimental values, at low temperatures the agreement is not satisfactory. However, the validity of applying the theory of Fan and Radkowsky to a material where the effective mass is large is somewhat doubtful. There is also the probability that there are piezoelectrically active acoustical modes which are important below 150°K.<sup>21</sup> This has been pointed out by Piper, Johnson, and Marple<sup>22</sup> to explain the failure of the theory to account for the temperature dependence of the band gap in ZnS in the region below 150°K.

<sup>21</sup> H. J. G. Meijer and D. Polder, Physica **19**, 225 (1953).

<sup>22</sup> W. W. Piper, P. O. Johnson, and D. T. F. Marple, J. Phys. Chem. Solids **8**, 457 (1959).

## Maser Oscillations at 0.9 and 1.35 Microns in CaWO<sub>4</sub>:Nd<sup>3+</sup>

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Previous reports have described optical maser oscillation at  $\sim 1.06 \mu$  from Nd<sup>3+</sup> in CaWO<sub>4</sub>. Oscillation occurs in  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transitions, the terminal state lying  $\sim 2000 \text{ cm}^{-1}$  above the ground state. The present note reports maser oscillation in  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$  transitions, the terminal states lying  $\sim 4000 \text{ cm}^{-1}$  above the ground state, and in  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  transitions, the terminal state lying  $471 \text{ cm}^{-1}$  above the ground state. Attempts to obtain maser oscillation at  $\sim 5 \mu$  in transitions between  ${}^4I$  multiplets were unsuccessful. It is concluded that these transitions are predominantly nonradiative.

### INTRODUCTION

PREVIOUS publications<sup>1-3</sup> have described details of optical maser oscillation at  $\sim 1.06 \mu$  arising from  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transitions of Nd<sup>3+</sup> in CaWO<sub>4</sub>. The terminal state for these transitions,  ${}^4I_{11/2}$ , lies  $\sim 2000 \text{ cm}^{-1}$  above the ground state. The present note reports maser oscillation in  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$  transitions, the terminal states lying  $\sim 4000 \text{ cm}^{-1}$  above the ground state, and in  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  transitions, the terminal state lying  $471 \text{ cm}^{-1}$  above the ground state.

When irradiated by white light, the trivalent neodymium ion in CaWO<sub>4</sub> produces strong infrared fluorescence consisting of three groups of lines centered at 0.9, 1.06, and  $1.35 \mu$ . The emission corresponds, respectively, to transitions from  ${}^4F_{3/2}$  to the  ${}^4I_{9/2}$ ,  ${}^4I_{11/2}$ , and  ${}^4I_{13/2}$  multiplets of the ground term. Since for all transitions the  $\sigma$  spectrum ( $E$  vector perpendicular to  $c$  axis) coincides with the axial spectrum (emitted beam parallel to  $c$  axis), the transitions are electric dipole.

The strongest emission, preferred for maser oscillation, is  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ , but with selective feedback by means of multiple layer dielectric reflectors, oscillation may be obtained in transitions to either  ${}^4I_{13/2}$  or  ${}^4I_{9/2}$ .

### ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ TRANSITIONS

The polarization of the  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$  emission (Na<sup>+</sup> compensation) is shown in Fig. 1. Maser transitions and their threshold energies (as measured by the electrical input to an FT 524 xenon lamp) are indicated in the figure. At room temperature, maser oscillation is obtained in the  $\pi$  line at  $1.339 \mu$  ( $7467 \text{ cm}^{-1}$ ). At 77°K, oscillation is observed in three lines at  $1.337 \mu$  ( $7478 \text{ cm}^{-1}$ ),  $1.345 \mu$  ( $7435 \text{ cm}^{-1}$ ), and  $1.387 \mu$  ( $7210 \text{ cm}^{-1}$ ). The low-threshold line at  $1.337 \mu$  has a width of  $6.4 \text{ cm}^{-1}$  at 77°K and  $2.4 \text{ cm}^{-1}$  at 20°K. The line at  $1.345 \mu$  is of about equal intensity, but has a width of  $6.9 \text{ cm}^{-1}$  at 77°K and  $3.3 \text{ cm}^{-1}$  at 20°K; therefore, oscillation occurs at a slightly higher threshold.

With the aid of absorption data, an energy level diagram identifying the  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$  transitions and their polarization is derived in Fig. 2. Several lines seen in fluorescence (Fig. 1) are believed to be satellites and are not included in Fig. 2. The location of six of the

<sup>1</sup> L. F. Johnson and K. Nassau, Proc. I.R.E. **49**, 1704 (1961).

<sup>2</sup> L. F. Johnson, G. D. Boyd, K. Nassau and R. R. Soden, Phys. Rev. **126**, 1406 (1962).

<sup>3</sup> L. F. Johnson, J. Appl. Phys. (to be published); Quantum Electronics Conference, Paris, 1963 (to be published).