

## Sulfur Vacancy Mechanism in Pure CdS

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Experiments have been performed on the luminescence of spectrographically pure CdS under ultraviolet excitation at room temperature. Both green and red emissions are observed. The green emission at 5240 Å (2.38 eV) is attributed to direct recombination. The red emission at 7180 Å (1.72 eV) is described in terms of a phenomenological model proposed by Lambe and Klick. The variations in luminescent intensity of the green and red bands and simultaneously in the photoconductivity of the crystals can be very adequately described if the 7180 Å luminescence is attributed to the presence of sulfur vacancies.

### I. INTRODUCTION

RECENT studies<sup>1-3</sup> of the luminescence spectrum of CdS(Ag), ZnS(Ag), and pure ZnS have led to the conclusion that certain of the observed spectral bands may be attributed to the existence of sulfur vacancies in these materials. In particular, a 6200 Å band observed in CdS(Ag) at 77°K has been attributed to sulfur vacancies while a 7300 Å band results from silver impurities. However, in the series of experiments which has led to the postulation of the vacancy mechanism, "pure" crystals have, to the authors' knowledge, been employed in only a single reported investigation.<sup>3</sup>

Two alternative models have been proposed for the luminescence of sulfides activated with impurities such as silver. Schön<sup>4</sup> and Klasens<sup>5</sup> have described the impurity states as ionized acceptor levels and attribute the luminescence to the capture of a conduction electron by a hole trapped at the acceptor level. Alternatively, Lambe and Klick<sup>6</sup> and Lambe<sup>7</sup> have correlated the results of their investigation of the 6200 Å band observed in CdS(Ag) at 77°K with a somewhat different phenomenological model. They ascribe the band to silver impurity states which act as vacant donor levels and consider the trapping of a hole at such a level to result in a radiative transition which gives rise to the observed luminescence. No mention is made of a 7180 Å emission.

The evidence presented by Lambe and Klick appears to leave little doubt concerning the donor nature of the centers responsible for the luminescence which they investigated in CdS(Ag). However, van Gool<sup>1,2</sup> and more recently Melamed<sup>3</sup> have objected to the assumption that substitutional silver is responsible for the proposed donor levels. van Gool has described an extensive investigation of the luminescence at low temperature in ultraviolet irradiated CdS(Ag). Two bands were observed at 77°K, with maxima at 6200 Å

and 7300 Å. High silver concentration and low co-activator (Ga or Cl) concentration promoted the short-wave emission, while with equal concentrations of silver and coactivator, only the 7300 Å band was observed. Using a series of mixed crystals, ZnCdS(Ag), it was shown that the 6200 Å and 7300 Å emissions in CdS(Ag) correspond to emissions at 3920 Å and 4350 Å, respectively in ZnS(Ag). van Gool has suggested that the 6200 Å band in CdS(Ag) and the 3920 Å band in ZnS(Ag) may be attributed to interstitial silver or sulfur vacancies.

Subsequently, Melamed has described an experiment with pure ZnS at 77°K and 3023 Å excitation and reported observing an emission band at 3950 Å. The band was also observed in specimens of ZnS(Cl) and ZnS containing 0.0001% copper without chloride. In view of these results, Melamed attributes the 3920 Å emission observed by van Gool in ZnS(Ag) to sulfur vacancies rather than to silver. He also concludes that the same mechanism is responsible for the 6200 Å emission investigated in CdS(Ag) by van Gool and by Lambe and Klick.

Experiments designed to study the room temperature luminescence of spectrographically pure CdS excited with ultraviolet radiation have recently been performed at these laboratories. The results, as will be shown, can be correlated in terms of the phenomenological model of Lambe and Klick. Furthermore, because of the purity of our crystals, it is not possible to attribute our observed 7180 Å luminescence to impurities. It is, therefore, proposed that the mechanism responsible for this band is one involving a sulfur vacancy.

### II. EXPERIMENTAL METHOD

The CdS specimens employed in these experiments were in the form of single crystals, grown by a vaporization-crystallization method first reported by Czyzak *et al.*<sup>8</sup> and recently described in more detail by Boyd and Sihvonen.<sup>9</sup> The crystals, when analyzed spectrographically, exhibited no uniformity in impurity con-

<sup>1</sup> W. van Gool and H. A. Klasens, *J. phys. radium* **17**, 664 (1956).

<sup>2</sup> W. van Gool, *Philips Research Repts.* **13**, 157-166 (1958).

<sup>3</sup> N. T. Melamed, *Phys. Rev.* **107**, 1727 (1957).

<sup>4</sup> M. Schön, *Z. Physik* **119**, 463 (1942).

<sup>5</sup> H. A. Klasens, *Nature* **158**, 306 (1946).

<sup>6</sup> J. Lambe and C. C. Klick, *Phys. Rev.* **98**, 909 (1955); *J. phys. radium* **17**, 663 (1956).

<sup>7</sup> J. Lambe, *Phys. Rev.* **98**, 983 (1955).

<sup>8</sup> Czyzak, Craig, McCain, and Reynolds, *J. Appl. Phys.* **23**, 932 (1952).

<sup>9</sup> D. R. Boyd and Y. T. Sihvonen, *J. Appl. Phys.* (to be published).

tent. Some contained no detectable impurities,<sup>10</sup> while others contained one or more of the following residual impurities which, when present at all, had concentrations no greater than indicated here: 0.0001% Mg, 0.0008% Si, and 0.0001% Cu. In particular, if silver was present, it was in concentrations of less than  $2.5 \times 10^{-5}\%$ .

In addition to direct visual observations of the crystals under ultraviolet, three experiments were performed: (1) determination of the luminescent spectrum under ultraviolet excitation, (2) variation in the spectrum with intensity of the excitation, and (3) variation of photoconductivity with intensity of excitation. These experiments were performed using a one-meter Bausch and Lomb double-grating-type monochromator, modified for use as a spectrometer with a resolving power of 15 Å/mm. In obtaining the spectrum and its variation with excitation, the CdS single crystal (at room temperature) was mounted on the entrance slit of the monochromator. A Corning 3-73 filter was placed after the crystal to prevent addition to the scattered light by the transmitted ultraviolet exciting radiation. This filter also served to prevent exposure of the photographic plate by the second order of this radiation. The crystal was illuminated with 3650 Å radiation from a Shannon Company ultraviolet lamp, with a filter placed between the source and the crystal in order to remove long-wavelength components, in particular a strong 7350 Å component, from the radiation incident onto the crystals. The spectra were registered by Eastman Kodak I-L photographic plates using exposure periods ranging from 10 to 30 minutes. For the photoconductivity experiments, the crystals were mounted as described above. In addition, however, contacts were made to the crystals employing No. 194

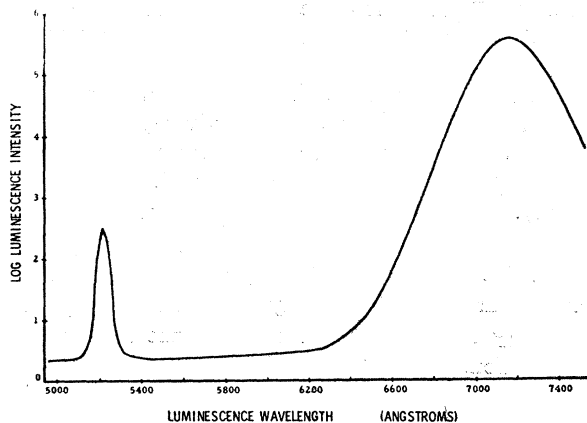


FIG. 1. Luminescent spectrum of CdS at room temperature, indicating both red and green emission. Crystal excited by 3650 Å radiation.

<sup>10</sup> Impurities, if present, were at a level lower than that indicated by C. E. Harvey, in *A Method of Semiquantitative Spectrographic Analysis* (Applied Research Laboratories, Glendale, 1947), pp. 75-79.

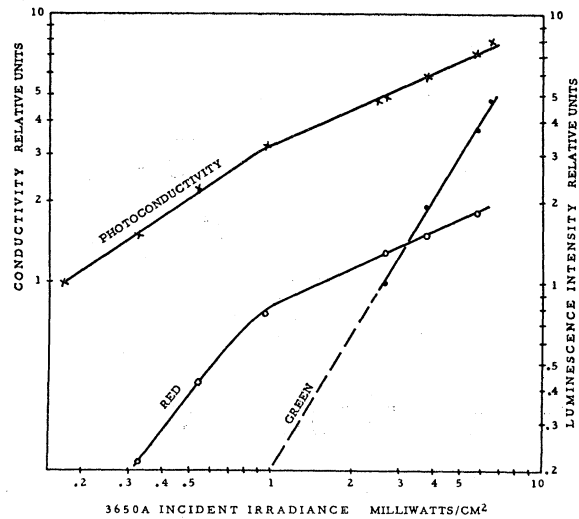


FIG. 2. Variation of conductivity and of red and green luminescence with intensity of 3650 Å radiation for CdS at room temperature. Green emission appears as the red-emitting centers saturated. Crystal conductivity changes abruptly when this occurs.

“Dag” dispersion. The contacts were attached to a voltage source and a sensitive microammeter.

### III. EXPERIMENTAL RESULTS

Direct visual observations of the crystals under ultraviolet illumination indicate striking differences in their behavior with increasing intensities. Some glow only red up to the maximum (6-mw/cm<sup>2</sup>) ultraviolet intensity available with the source. Others, when irradiated at low intensity, glow red, the luminescent intensity increasing with excitation intensity until a green luminescence appears. At higher excitation intensities, these crystals simultaneously glow red and green giving an orange-like luminescence. Finally, a third type of crystal exhibits only green luminescence at all intensities. Thus, some crystals, which exhibit only red luminescence at low excitation intensities, may be made to glow green at sufficiently high excitation. Those which glow only green at low excitation have never been observed to exhibit a red glow at any higher ultraviolet intensity. It should be noted that it has not been possible to correlate this behavior with residual impurity content.

Monochromator studies of crystals which can be made to luminesce both red and green result in a spectrum of the general form displayed in Fig. 1. The rather narrow green band at 5240 Å is attributed to direct recombination since the value 2.38 eV agrees closely with measurements of the forbidden gap in CdS at room temperature.<sup>11</sup> In addition to the green emission, a very broad band with a peak at about 7180 Å (1.72 eV) is also observed. This red band will be of primary interest in the present discussion and is

<sup>11</sup> R. H. Bube, Proc. Inst. Radio Engrs. 43, 1836 (1955).

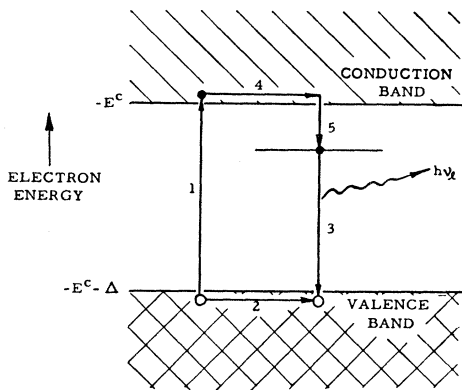


FIG. 3. Schematic representation of model proposed for red luminescence in CdS (after Lambe and Klick<sup>6</sup>).

the one which we attribute to the action of the sulfur vacancies.

Photoconductivity measurements, Fig. 2, on crystals glowing both red and green indicate that they are relatively sensitive at low ultraviolet intensities when the crystals exhibit primarily red luminescence. However, at some ultraviolet irradiation level there is a transformation to a lesser sensitivity which remains substantially constant with further increases in excitation intensity.

The general behavior of the luminescent spectrum as a function of ultraviolet intensity, also displayed in Fig. 2, is as expected from the visual observations. It was found that at low exciting intensities the red luminescence dominates a weak green. As the incident irradiation increases, the red emission intensity increases more rapidly than linearly until a saturation occurs. At the incident intensity for which this saturation begins to occur, the green luminescence begins to appear with marked intensity. This green emission increases more rapidly than linearly with ultraviolet intensity.

#### IV. CORRELATION OF RESULTS

The experimental results described above can be correlated on the basis of the model proposed by Lambe and Klick,<sup>6</sup> if one includes one additional assumption. The basic model, shown schematically in Fig. 3, together with the assumption that the luminescent recombination centers can be saturated is fully adequate to explain our experimental results. The behavior of the three different types of luminescing crystals is explained as follows. The crystals that glow only red contain a concentration of centers so great that the red transition cannot be saturated with the available ultraviolet intensity. Those which glow only green contain a concentration of centers which is so low that only direct recombination emission is observed. In the crystals which first exhibit red emission and then green emission, the concentration of centers is such that they can be saturated for a given rate of hole

production. At higher rates, only the direct recombination mechanism resulting in green emission is available.

In addition, it has also been ascertained that the dark conductivities in our red-only crystals are some 2 to 3 orders of magnitude higher than those in green-only crystals. This is considered to be added evidence for the donor nature of the centers responsible for the observed 7180 Å luminescence since these would be present in red-only crystals in much higher concentrations than in those which glow only green.

#### V. SUMMARY AND CONCLUSIONS

In view of the results presented here for CdS, it would appear that while the model proposed by Lambe and Klick is sufficient to correlate the experimental data, the assumption of a sulfur vacancy mechanism is required to explain the observed 7180 Å emission in pure CdS at room temperature. In CdS crystals containing sulfur vacancies, two electrons will be trapped near each vacancy at absolute zero with no incident radiation, in order to insure charge neutrality of the crystal. At higher temperatures, and assuming such sites to introduce donor levels it is to be expected that a few sites will lose an electron to the conduction band, resulting in a small dark current whose magnitude is a function of vacancy concentration. Sites which still contain both electrons will act as deep traps for holes formed in the valence band by the absorption of ultraviolet radiation. The 7180 Å radiation emitted in the trapping process is the observed red luminescence. Under sufficiently intense excitation it is assumed that an equilibrium is established in which each vacancy site contains only one electron, since the energy of the single remaining electron will be quite low and a site with one electron missing will repel additional holes. For incident intensities beyond the value required to establish this condition, electrons and holes begin to recombine directly, giving rise to the observed green emission.

Finally, the authors wish to point out that while the investigations of activated-coactivated CdS phosphors have yielded considerable luminescence data, an uncertainty arises as to the role played by a sulfur vacancy. This uncertainty has originated because of the complex nature of these mixtures, and it appears much more reasonable to study the effects of such vacancies in simple high-purity crystals deviating only in primary stoichiometry as has been the case in this investigation.

#### ACKNOWLEDGMENTS

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