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Low-Temperature Luminescence and Absorption of CdS

L. R. FURLONG AND C. F. RAVILIOUS
United States Naval Research Laboratory, Washington, D. C.

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Measurements of the emission and absorption of CdS single crystals have been made at several temperatures. At 4°K a set of emission lines in the range 4850–5020 A has been found. A study of these lines together with observations at other temperatures suggests that they are emitted by a system consisting of the combination of a gas and CdS, the gas being adsorbed on the crystal.

INTRODUCTION

THE luminescence of CdS at low temperatures has been studied by several workers. At 93°K Kroeger[1] found several emission bands in the range 5100–5600 A and other bands at shorter wavelengths. At 77°K Klick[2] found several emission bands in the range 5000–5600 A and at 4°K he found a set of bands in the same region together with some diffuse structure at shorter wavelengths. At 4°K one of us[3] found three less intense bands lying among Klick's three most intense bands.

This paper is a result of further investigation of the luminescence and absorption of CdS single crystals. At 4°K we have found a set of emission lines, the half-width being of the order of 1 A, and some similarly narrow absorption lines. In connection with this we have investigated the emission and absorption at other temperatures. At 300°K our study of the single emission band leads us to suggest that it is associated with the line emission at 4°K.

The luminescence measurements were made by photographing the emission of a single crystal with a Hilger medium glass spectrograph. The crystal was excited by ultraviolet radiation from a one-kilowatt Westinghouse mercury vapor lamp Type SAH 1000 A filtered with a Corning 7-54 filter. The absorption measurements were made by similarly photographing the light transmitted by a single crystal which was irradiated by a tungsten-filament lamp.

TABLE I. Low-temperature luminescence of CdS.

Green bands at 4°K λ(A)	Blue bands at 4°K λ(A)	Bands at 77°K λ(A)
5100	4853	4840
5133	4867	4870
5182	4886	4885
5212	4907	4946
5267	4913	5027
5290	4925	5129
5350	4940	5214
5445	4962	5300
5530	4990	5390
5630	5004	5478
	5020	5572

EXPERIMENTAL RESULTS

A. At 4°K

The emission of a CdS single crystal at 4°K is shown in the first two columns of Table I and in Fig. 1(a).

Two of the green bands listed in Table I, namely 5212 A and 5290 A, have been obscured in Fig. 1(a) by the over-exposure of the 5182, 5267, and 5350 A bands. The over-exposure of these green bands was necessary in order to detect the much less intense blue lines on the same plate. The half-width of these bands is of the order of 10 A, as reported in reference 2, and have fairly regular spacing.

The blue emission lines at 4°K have a half-width of the order of 1 A and lack the regular spacing characteristic of the green bands. They are also much less intense than the green bands. Furthermore, these lines can be restored to full intensity by means of a short exposure to air after their intensity has been reduced by simultaneously baking and pumping on the crystal.

The absorption spectrum at 4°K also has very interesting characteristics. Gross and Karryev[4] reported a narrow absorption line at 4869 A for a cadmium sulfide single crystal at 73°K. At 4°K we have found absorption lines, of approximately 1 A half-width, at 4825, 4852, and 4867 A. Of the three absorption lines the weakest is at 4825 A and there is a very weak emission corresponding to this at a slightly longer wavelength. The absorption line at 4852 A seems to correspond to the emission line at 4853 A. The most

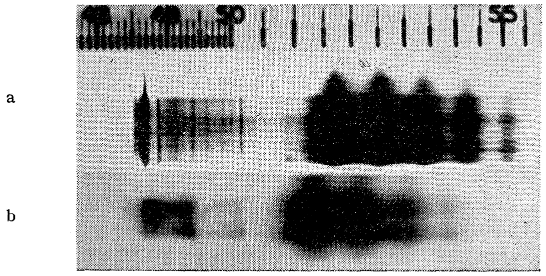

FIG. 1. Luminescence of CdS single crystal (a) at 4°K; (b) at 77°K. The scale at the top is the wavelength scale (in units of 100 A).

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[1] F. A. Kroeger, Physica **7**, 1 (1940).
[2] C. C. Klick, Phys. Rev. **89**, 274 (1953).
[3] L. R. Furlong, Phys. Rev. **95**, 1086 (1954).
[4] E. F. Gross and N. A. Karryev, Doklady Akad. Nauk S.S.S.R. **84**, 471 (1952).

interesting and most intense of the absorption lines is at 4867 A. As shown in Table I and Fig. 1(a) this is also the wavelength of the most intense of the blue emission. This phenomenon is reminiscent of resonance radiation, characteristic of gases. However, this suggestion is made with reservations because of the possibility of a 1 A error.

We found these three absorption lines to be superimposed on an absorption continuum which for unpolarized incident radiation is maximum and constant at wavelengths shorter than 4850 A and decreases rapidly at longer wavelengths. In connection with the absorption continuum, Gobrecht and Bartschat[5] observed that the position of the absorption edge of cadmium sulfide crystals at 293°K and at 93°K is a function of the direction of polarization of the incident light with respect to the *C*-axis of the crystal. We have observed the same behavior of the absorption edge at 4°K. When the incident light is linearly polarized with the electric vector parallel to the striations in the crystal platelet (and, therefore, parallel to the *C*-axis[5]) the absorption continuum is the same as when the incident radiation is unpolarized. However, when the incident light is polarized perpendicular to the striations the longest wavelength of maximum absorption moves from 4850 A to 4874 A.

B. At 77°K

The emission spectrum of a cadmium sulfide single crystal at 77°K is shown in the third column of Table I and in Fig. 1(b). For CdS:Ag at 77°K Klick[6] has obtained structure in the 4800–5000 A region and Kroeger[1] found some bands in this region at 93°K.

In this case we found absorption lines at about 4840 A and 4870 A. For the incident radiation unpolarized or polarized parallel to the *C*-axis the longest wavelength of maximum absorption is at 4880 A whereas this occurs at 4910 A for perpendicularly polarized incident radiation.

C. At 300°K

We found a single green emission band maximized at 5077 A with a half-width of 160 A. We also obtained the absorption continuum. The emission band lies within the absorption continuum except for a small portion of the long-wavelength tail. This fact might indicate that this emission is surface emission but not necessarily since the emission might originate within the crystal and be absorbed to a large extent before reaching the surface. However, other observations do indicate this to be surface emission. For example, gentle scraping of the crystal suppresses this emission as does ionizing the gas surrounding the crystal. Furthermore, microscopic examination of the emitting crystal indicates surface emission. We determined the position of the peak of this emission band as a function of temperature, with the results given in Table II. We have not included entries at 77°K and 4°K since at these temperatures we have structure rather than a single band. However, it is interesting that the trend of the peak is toward that portion of the spectrum occupied by the blue set of emission lines at 4°K and that the spread of the blue lines (that is, from 4853 A to 5020 A) is approximately the half-width of the single band at room temperature.

TABLE II. Position of maximum of the luminescence band as a function of temperature.

T (°K)	λ(A)
300	5077
273	5065
195	4980
147	4960
113	4895

DISCUSSION

The characteristics of the blue set of emission lines at 4°K are: (1) narrowness, the half-width being of the order of 1 A as compared to a half-width of the order of 10 A for the green band; (2) lack of regular spacing such as was found for the green bands; (3) a much lower intensity, in general, than that of the green bands; (4) an apparent connection with the green emission band at 300°K, which we have ascribed to the surface; (5) the restoration of these lines to full intensity by means of a short exposure to air after the intensity has been reduced by simultaneously baking and pumping on the crystal; (6) the appearance of an absorption line apparently at the position of the 4867 A emission line.

These characteristics suggest that one explanation for these emission lines is that they are representative of the combination of a gas and cadmium sulfide, the gas being adsorbed on the crystal. It is not unreasonable to suppose that the electronic states of a gaseous system might be modified by a dielectric on which it is adsorbed. The temperature shift of the emission may be associated with the same causes which account for the temperature variation of the forbidden energy gap in the crystal. The structure at 4°K, as contrasted with the single band at 300°K, could arise from less coupling with the lattice vibrations as the temperature is lowered.

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[5] H. Gobrecht and A. Bartschat, Z. Physik **136**, 224 (1953).

[6] C. C. Klick, J. Opt. Soc. Am. **41**, 816 (1951).

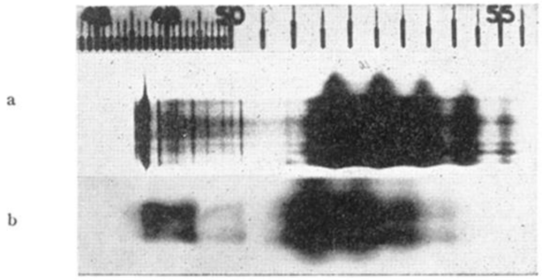

FIG. 1. Luminescence of CdS single crystal (a) at 4°K; (b) at 77°K. The scale at the top is the wavelength scale (in units of 100 A).