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Change in Structure of Blue and Green Fluorescence in Cadmium Sulfide at Low Temperatures

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The two fundamental fluorescences observed in cadmium sulfide crystals subjected to ultraviolet excitation at low temperatures are classified according to wavelength. Photographs of the two fluorescences at 4.2°K and 77°K are given, and their structures are compared. Experimental evidence on the change in structure of the green emission near 5130A between 4.2°K and 77°K is presented and used to confirm an explanation for the apparent "green" shift in cadmium sulfide proposed by D. G. Thomas and J. J. Hopfield.

TWO fundamental fluorescences have been observed in cadmium sulfide crystals subjected to ultraviolet excitation at low temperatures.[1,2] One has been described as green fluorescence, the other as blue fluorescence. Recently one of us reported on the marked difference in temperature dependence of the two fluorescences between 77°K and 300°K.[3] It is the purpose of this paper to classify the so-called blue and green fluorescence, compare their structure at 4.2°K and 77°K, and report in detail on the gradual change in structure of several components of the green fluorescence near 5130 A as the crystal temperature changes from 4.2°K to 77°K.

The fluorescence from two different types of cadmium sulfide platelets, thickness $\sim 10\,\mu$, was photographed at 77°K and 4.2°K. One platelet, subjected to ultraviolet excitation, showed both the blue and green fluorescence, while the other platelet, under similar excitation, showed the blue fluorescence. Figure 1 shows the fluorescence spectrums photographed at 77°K and 4.2°K for the "blue-green" and "blue-only" CdS platelets, using a Jarrell-Ash spectrograph having a linear dispersion of 7 A/mm. Photographs *A* and *B* show the fluorescence from the "blue-green" platelet at 77°K and 4.2°K, respectively. Photographs *D* and *C* show the fluorescence from the "blue-only" platelet at 77°K and 4.2°K, respectively. Proper orientation of the four separate exposures in Fig. 1 has been obtained by aligning the mercury line $\lambda = 4358.3$ A on each photograph.

By comparing photographs of the "blue-green" fluorescence and the "blue-only" fluorescence, both at 4.2°K, (*B* and *C*, Fig. 1) it is possible to classify by wavelength the green fluorescence and the blue fluorescence. The results of this classification are shown in Table I where G_1—G_{11} denotes the components of the green fluorescence and B_1—B_4 denotes the components of the blue fluorescence. Further analysis of the four photographs yields the following results.

1. The fluorescence at 77°K (*A* and *D*, Fig. 1) is characterized by rather broad lines, some of which show a gradual shading in intensity up to a definite cutoff point, reminding one of the bands observed in molecular spectra.

2. The fluorescence at 4.2°K (*B* and *C*, Fig. 1) is characterized by sharper lines with a more complex structure. The blue fluorescence (B_1—B_4) occurs as a series of triplets as indicated on photograph *B*. The triplet sets B_2, B_3, and B_4 are separated from each other by approximately 0.04 ev which corresponds closely to the longitudinal optical phonon energy. Grillot, Gross, Grillot, and Razbirin[4] have previously observed triplets in blue fluorescence but they did not report triplet B_4. In addition, one of the lines they report as blue fluorescence, G_1, has been attributed to green fluorescence according to our classification.

3. Photographs *A* and *B*, Fig. 1 indicate that the blue-green fluorescence at 77°K not only changes its

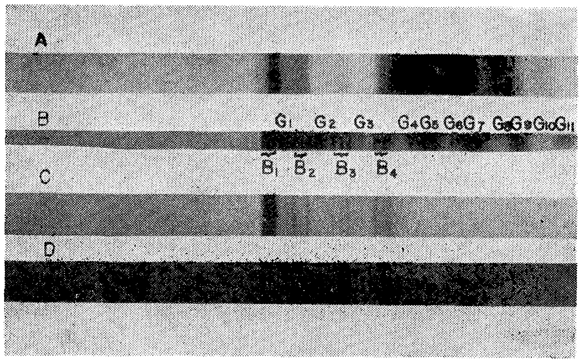

FIG. 1. Blue and green fluorescence observed in pure CdS platelets at 77°K and 4.2°K. A shows "blue-green" at 77°K, *B* shows "blue-green" at 4.2°K, *C* shows "blue-only" at 4.2°K and *D* shows "blue-only" at 77°K.

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[1] F. A. Kroger, Physica **7**, 1 (1940).

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

[3] D. C. Reynolds, Phys. Rev. **118**, 478 (1960).

[4] M. Bancie-Grillot, E. F. Gross, E. Grillot, B. S. Razbirin, Optika i Spektroskopiya **5**, 461 (1959).

structure but apparently shifts as a result of lowering the crystal temperature to 4.2°K. The blue fluorescence (B_1—B_4) is found to shift toward shorter wavelengths for the temperature change from 77°K to 4°K. Although the green fluorescence appears to shift toward longer wavelengths for the same temperature change subsequent investigation described below shows that in reality lines G_5, G_7, G_9, and G_{11} which are prominent at 4.2°K disappear as the temperature is increased and lines G_4, G_6, G_8, and G_{10} which are sharp and relatively weak at 4.2°K develop into the broad green lines at 77°K, as observed in photographs *A* and *B*, Fig. 1.

In an attempt to study the details of the temperature "shift" of the green fluorescence between 4.2°K and 77°K, the following experiment was performed. A "blue-green" platelet was attached with silver paint to an aluminum rod which was immersed in liquid helium, all of which was contained in the inner Dewar of a double Dewar arrangement. The liquid helium was allowed to evaporate from the inner Dewar, and as a result the crystal temperature increased gradually from 4.2°K to 77°K. A Bausch and Lomb grating monochromater using a IP28 photomultiplier tube was used to monitor the positions of the green lines G_4 and G_5 as the temperature increased. A copper-constantan thermocouple fastened to the aluminum rod adjacent to the crystal was used to record the temperature rise. The temperature measurements were not taken at equilibrium conditions, and thus a temperature lag between thermocouple and crystal may have existed. The results of the measurement are shown in Fig. 2. It can be seen that line G_5 rapidly disappears with increase in temperature and line G_4 increases rapidly in intensity and width, developing into the first of the green bands at 77°K. This shows that the broad lines at 77°K do not shift positions towards longer wavelengths as the crystal is cooled to 4.2°K.

TABLE I. Classification by wavelength of blue and green fluorescence in cadmium sulfide.

Blue (A)	Green (A)
4853	4885—G_1
4863—B_1	4959—G_2
4871	5037-G_3
	5129—G_4
4913	5179—G_5
4925—B_2	5211-G_6
4938	5254—G_7
	5298—G_8
4986	5341—G_9
5002—B_3	5382—G_{10}
5016	5436—G_{11}
5065	
5082—B_4	
5092	

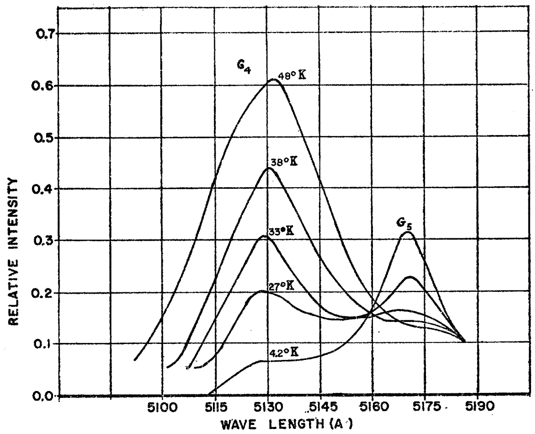

FIG. 2. Relative intensity of lines G_4 and G_5 as temperature increases above 4.2°K.

To account for this apparent "shift" in the green emission towards longer wavelength Thomas and Hopfield[5] offered two possible explanations. The first explanation assumes this green emission to be the result of the recombination of electrons in minima not at $K=0$ with trapped holes. The shift toward longer wavelength is explained by assuming that these off-axis minima move down relative to the $K=0$ minima as the temperature is decreased. The second explanation assumes that a bound state of an electron exists in the vicinity of a trapped hole. At 77°K the recombination causing the green emission would take place from the unbound states, e.g., conduction band to trapped hole, while at 4.2°K the recombination would take place from the bound states, e.g., bound state of electron to the trapped hole. The energy difference between the two recombination processes would account for the apparent shift in wavelength.

The first possibility requires that the wavelength of the green emission observed at 77°K change gradually towards longer wavelengths as the crystal is cooled to 4.2°K. The data clearly indicate that this is not the case. The experimental evidence contained in Fig. 2 is in agreement with the second possibility and thus appears to confirm this explanation for the apparent green shift in cadmium sulfide.

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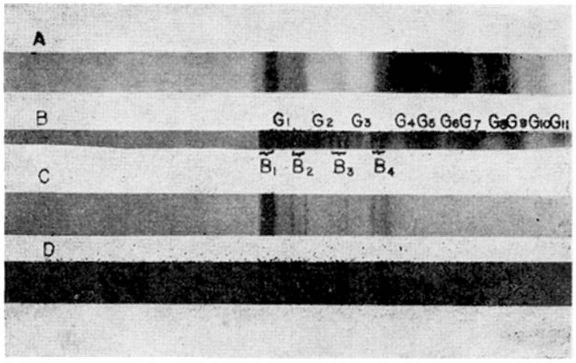
[5] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).



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