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Temperature Dependence of Edge Emission in Cadmium Sulfide

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The temperature dependence of the blue and the green emission in cadmium sulfide has been investigated in the temperature range from 77°K to 300°K. The blue emission shifts to longer wavelengths as the temperature is increased above 77°K with a temperature coefficient of 4.9×10^{-4} ev/°C. The intensity of the green emission falls off exponentially above 77°K with very little shift in the spectral position of the green peaks.

TWO fundamental emissions[1,2] are observed in cadmium sulfide at low temperatures. One occurs in the blue region of the spectrum, the other in the green. It is the purpose of this paper to report on the temperature dependence of these emissions between liquid nitrogen temperature and room temperature.

In studying the emission a large number of platelet type crystals were investigated. Many of them showed intense green emission at room temperature, while quite a number of them showed only blue emission at 77°K, the green emission being absent. A large number showed both the blue and the green emission at 77°K. The blue emission in all crystals at 77°K showed three well defined peaks at 4880A, 4927A, and 5012A. The platelets were grown from the vapor phase[3] and vary in thickness from $<1\mu$ to approximately 100μ. The "*C*" axis is contained in the plane of the plate. The emission was measured on the as grown surfaces.

The temperature dependence of the blue emission is shown in Fig. 1. The emission spectra was determined from a platelet a few millimeters on a side and approximately 20μ in thickness. The crystal was excited with a *H*100-*SP*4 mercury lamp, filtered to eliminate the visible, and the emission detected with a Bausch & Lomb grating monochromator equipped with a 1*P*28 photomultiplier tube. The emission spectra in Fig. 1 were normalized to constant intensity of the maximum for purposes of more conveniently showing the shift in the peak toward longer wavelengths as the temperature was increased. The intensity of the emission decreases as the temperature is increased; the normalization was accomplished by opening the slits of the monochromator to give constant peak intensity as the temperature was increased. The slits at liquid nitrogen temperature were set at 0.04 mm and were opened to approximately 0.1 mm at room temperature. Before using this normalizing procedure it was verified that changing the slit width as described above did not shift the position of the peaks. It should also be pointed out that structure in the emission at higher temperatures could not be observed even at the narrowest slit setting except for the indication of the second peak at −126°C shown in Fig. 1. Associated with the short wavelength emission peak at 77°K is a strong photoconductive peak. The photoconductivity as a function of wavelength is shown superimposed in Fig. 1. The photoconductivity was excited with a *B*-*H*6 mercury vapor lamp as the source for the monochromator and the photocurrent was detected with a Model 210 Keithley electrometer. Another aspect of the blue emission is its shift to longer wavelengths as the temperature is increased. The temperature coefficient of the shift is 4.9×10^{-4} ev/°C. This is in agreement with the value given by Klick[4] for the temperature coefficient of the band edge determined from absorption measurements in the temperature range 77°–300°K. The first two peaks are separated by 0.024 ev. The second and third peaks are separated by approximately twice this energy, viz., 0.042 ev. This latter energy is very nearly equal to the longitudinal optical phonon energy of 0.038 ev.[5,6]

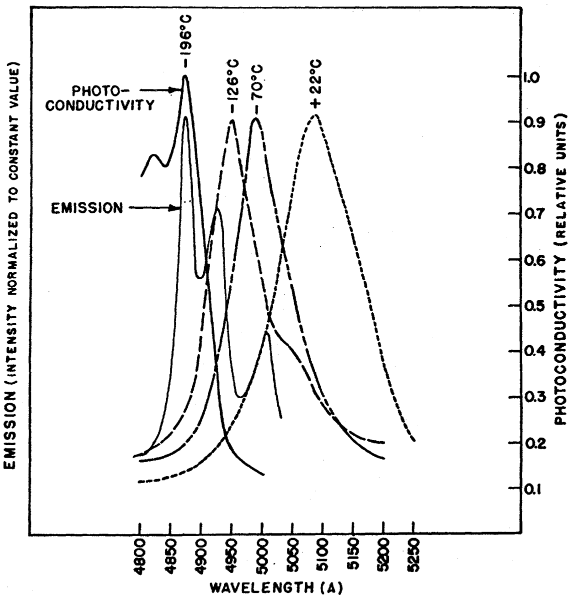

FIG. 1. Temperature dependence of blue emission in cadmium sulfide between 77°–299°K. Photoconductivity in the same crystal at 77°K is also shown.

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

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

[3] D. C. Reynolds and L. C. Greene, International Conference on Solid State Physics, Brussels, June, 1958 (unpublished).

[4] C. C. Klick, Phys. Rev. **89**, 274 (1953).

[5] J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).

[6] R. J. Collins, J. Appl. Phys. **30**, 1135 (1959).

These three peaks move together with temperature as an entity and their temperature dependence differs greatly from that of the green emission indicating that the two emissions arise from different origins.

Furlong and Ravilious have attributed this emission to gas adsorbed on the surface of the crystal.[7] This appears not to be the case. Though it is true that scraping the surface of the crystal suppresses the emission, it can subsequently be restored by etching. Also, if the emission is suppressed by scraping, it can be restored by cleaving off that surface of the crystal and exposing a new surface. It is also true that grinding or polishing destroys the green emission. This emission can also be restored by subsequent etching. Since the blue emission occurs at the band edge one would expect it to be strongly dependent on the surface condition of the crystal.

The decay of the intensity of the green emission with increasing temperature is shown in Fig. 2 and Fig. 3. In Fig. 2 the decay of the peak intensity of the 5140A peak is shown. Figure 3 shows the decay of the integrated intensity of the total green emission. The emission was measured on a platelet approximately 5 mm on a side and 40 μ thick. The points on the curve marked with an *X* were determined with the crystal mounted over an aperture in a copper block. The thermocouple was attached to the copper block and thus the temperature of the copper block was measured. In this type of measurement there is always an uncertainty as to whether the crystal is in temperature equilibrium with the copper block. Three check points were obtained by immersing the crystal in boiling oxygen, boiling nitrogen and freezing nitrogen. These points are marked with an *o* on the curve.

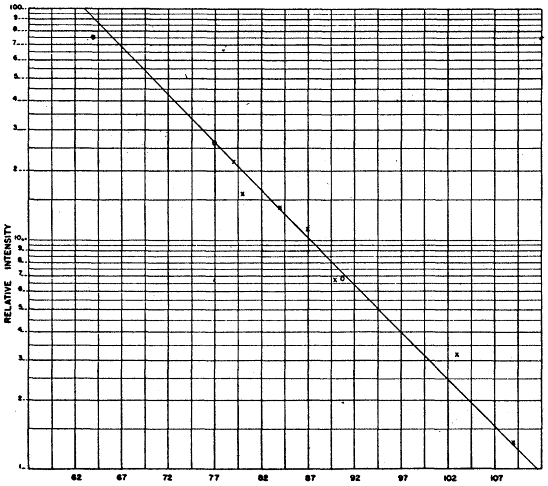

FIG. 2. Emission intensity as a function of temperature for the 5140A green line.

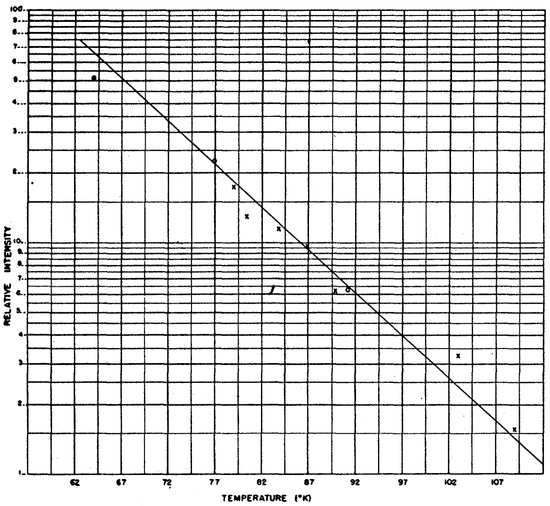

FIG. 3. Integrated intensity of the edge emission as a function of temperature in cadmium sulfide.

It appears that a change in the temperature dependence of the emission intensity may be occurring below liquid nitrogen temperatures suggesting that the measurements should be extended to liquid helium temperatures. The green emission disappears exponentially as the temperature is increased above 77°K. There is little shift in the position of the green peaks as the temperature is increased above 77°K, however, there is a shift to longer wavelengths as shown by Klick,[4] between 77°K and 4°K. This is in the opposite direction to the shift of the blue emission. This vast difference in the temperature dependence of the two emissions suggests that they may result from different minima in the conduction band. Thomas and Hopfield[8] have observed the temperature dependence of the emission in cadmium sulfide between 4°K and 77°K. They have presented two possibilities for explaining the shift of the green emission to longer wavelengths as the temperature is reduced from 77°K to 4°K. First they present the possibility of transitions occurring from minima in the conduction band not at $K=0$. The second possibility is that there exists a bound state of the electron in the vicinity of the trapped hole. Recently Boer and Gutjahr[9] have observed indirect transitions in absorption measurements providing additional evidence that minima away from $K=0$ are present. The disappearance of the green emission as the temperature is increased above 77°K, as well as the shift to shorter wavelengths as the temperature is increased above 4°K could then be explained by assuming that the off-axis minima move up relative to the $K=0$ minima as the temperature is increased, in agreement with Thomas and Hopfield's first hypothesis.

ACKNOWLEDGMENT

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[7] L. R. Furlong and C. F. Ravilious, Phys. Rev. **98**, 954 (1955).

[9] K. W. Boer and H. Gutjahr, Z. Physik **155**, 328 (1959).