

embarked on a systematic study of all rare earth activators in strontium sulfide. An attempt will be made to grow single crystals.

Part of this work was done while the author spent the summer at the Clarendon Laboratory, Oxford.

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Temperature Dependence of the Width of the Band Gap in Several Photoconductors

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The temperature dependence of the width of the forbidden band gap has been determined, between 90° and 400°K, for cadmium sulfide, cadmium selenide, cadmium telluride, and zinc selenide, by measurement of photosensitivity as a function of wavelength. The location of the maximum photosensitivity, often very sharp, at the wavelength corresponding approximately to the width of the band gap, makes this method very convenient for the determination. Structure exists in the photosensitivity maxima of cadmium sulfide and cadmium selenide, suggesting the existence of double conduction or valence bands.

INTRODUCTION

THE temperature dependence of the width of the forbidden gap of a semiconductor is commonly determined by measuring the dependence of the absorption on wavelength, at a number of different temperatures. Such measurements have been made by Kroeger,¹ Seiwert,² and Hoehler³ for cadmium sulfide. Their results indicate that the absorption-edge shifts to longer wavelengths at the rate of about 1 Å/°K for increasing temperature.

Because of the broadness of the absorption edge in most semiconductors, it is somewhat difficult to determine a width for the forbidden gap accurately, and hence to determine accurately the temperature dependence of the gap width. In many cases, such striving for greater accuracy may be pointless, because of an inherent lack of definition in the band edges themselves. But, at least experimentally, it is much simpler to determine a quantity which is very nearly equal to the width of the forbidden gap for photoconducting crystals, by measuring the photosensitivity as a function of wavelength. Most photoconducting crystals show a rather sharp maximum of photosensitivity at a wavelength corresponding closely to the width of the forbidden gap, as determined from measurements of absorption. Niekisch⁴ and Caspary and Mueser,⁵ have determined the temperature dependence of the forbidden gap for cadmium sulfide from measurements of photosensitivity as a function of wavelength. Their results also indicate approximately a 1 Å/°K shift in absorption edge.

The purpose of this paper is to present data on the variation of the width of the forbidden gap with temperature between 90° and 400°K, for crystals of cadmium sulfide, cadmium selenide, cadmium telluride, and zinc selenide.

EXPERIMENTAL

Materials

The preparation of single crystals of "pure" cadmium sulfide, cadmium selenide, and zinc selenide by S. M. Thomsen, by reaction between the elements in the vapor phase, has been described in a previous publication.⁶ The growth of crystals of cadmium telluride by D. A. Jenny and E. B. Lawton, by slow cooling from the melt, has also been previously reported.⁷

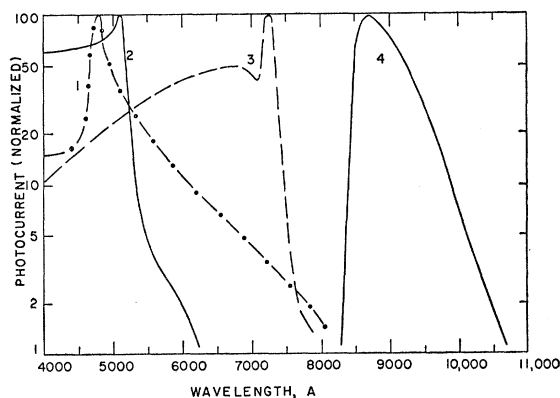


FIG. 1. Spectral curves of photosensitivity for (1) zinc selenide, (2) cadmium sulfide, (3) cadmium selenide, and (4) cadmium telluride, at room temperature.

¹ F. A. Kroeger, *Physica* **7**, 1 (1940).

² R. Seiwert, *Ann. Physik* **6**, 241 (1949).

³ G. Hoehler, *Ann. Physik* **4**, 371 (1949).

⁴ E. A. Niekisch, *Ann. Physik* **8**, 291 (1951).

⁵ R. Caspary and H. Mueser, *Z. Physik* **134**, 101 (1952).

⁶ R. H. Bube and S. M. Thomsen, *J. Chem. Phys.* **23**, 15 (1955).

⁷ D. A. Jenny and R. H. Bube, *Phys. Rev.* **96**, 1190 (1954).

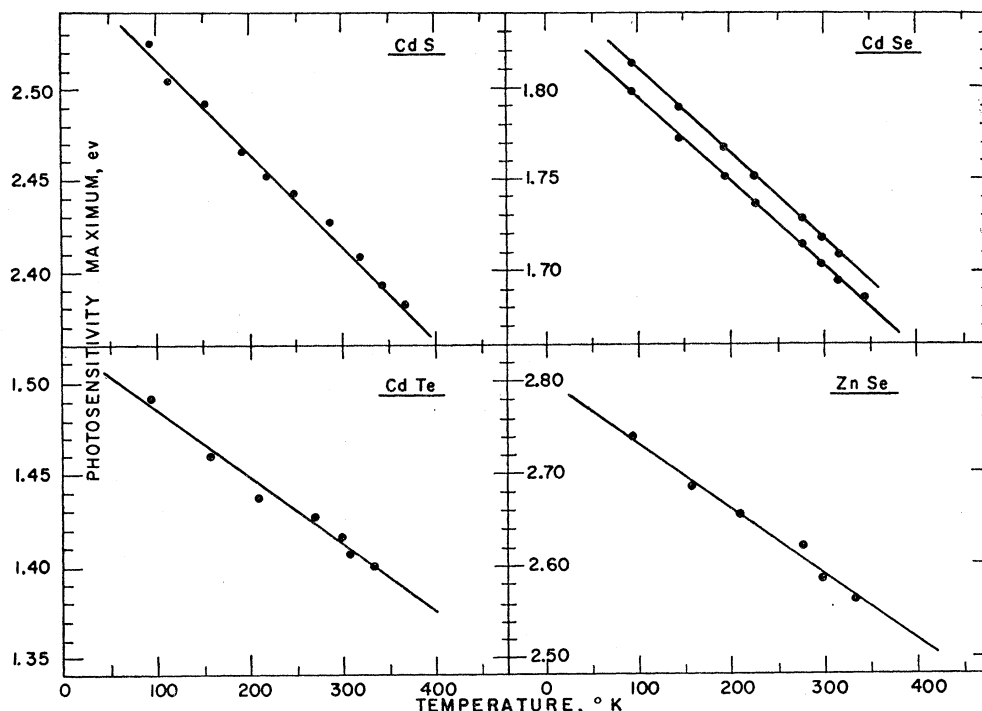


FIG. 2. The location of the photosensitivity maximum (or maxima) as a function of absolute temperature, for cadmium sulfide, cadmium selenide, cadmium telluride, and zinc selenide.

Electrical contact to the cadmium sulfide, cadmium selenide, and zinc selenide crystals was made using melted indium electrodes.⁸ The ends of the crystal of cadmium telluride were plated with nickel and copper, and then leads were soldered to the plated portions.

Measurements

Photosensitivity spectra were measured with a 500-mm Bausch and Lomb grating monochromator, using the photoconductivity *vs* temperature apparatus previously described.⁹ The highest resolution compatible with reliable measurements was used at all times; a resolution of 16.5 Å was used for all measurements on cadmium sulfide and low-temperature measurements on cadmium selenide, 33 Å for high-temperature measurements on cadmium selenide and all measurements on cadmium telluride, and 49.5 Å for all measurements on zinc selenide.

RESULTS

Temperature Dependence of Gap Width

Spectral curves of photosensitivity at room temperature are given for the four different crystals in Fig. 1. In plotting the curves, the data were corrected so as to indicate the photocurrent for an equal number of photons incident per second at any wavelength,

⁸ R. W. Smith and A. Rose, *Phys. Rev.* **92**, 857(A) (1953).

⁹ R. H. Bube, *J. Chem. Phys.* **23**, 18 (1955).

assuming a linear current-light relationship.¹⁰ All of the crystals show a sharp photosensitivity maximum except cadmium telluride, and even for this crystal the identification of the maximum is not difficult.

The decrease in photosensitivity for wavelengths shorter than the wavelength for maximum photosensitivity for cadmium sulfide, cadmium selenide, and zinc selenide, is probably due to the fact that radiation in this range is heavily absorbed in surface regions which have an intrinsically smaller photosensitivity than volume regions. In the case of the cadmium telluride crystal, it is probable that the very rapid decrease of photosensitivity for wavelengths shorter than the absorption edge is caused both by this effect, and also by a geometrical effect whereby the applied field is concentrated across a section of the crystal somewhat distant from the surface upon which the radiation is incident.

The location of the photosensitivity maximum is plotted in energy units in Fig. 2 for each of the four crystals, as a function of temperature. The constants involved in a linear relationship between band gap in electron volts and absolute temperature were derived

¹⁰ The assumption of a linear current-light curve is not justified for the cadmium selenide crystal, which has, for the light intensities used, a superlinear current-light dependence [see: R. H. Bube, paper in *Proceedings of the Conference on Photoconductivity* (John Wiley and Sons, New York, 1955)]. For this reason, the photosensitivity at longer wavelengths may be somewhat greater relative to that at shorter wavelengths than the curve in Fig. 1 for CdSe indicates.

from each of these plots by means of the method of least squares. Over this temperature range, an approximately linear relationship may also be derived between the wavelength corresponding to the absorption edge and the absolute temperature. These relationships are summarized in Table I.

Structure in the Photosensitivity Maximum

A detailed inspection of the photosensitivity maximum of cadmium sulfide, and of that of cadmium selenide (the two crystals for which the sharpness of the maximum and the resolution which could be used make such inspection meaningful), reveals that the photosensitivity maximum for both cadmium sulfide and cadmium selenide exhibits two components. The existence of such structure in the case of cadmium sulfide was suggested in the data previously reported by Klick.¹¹

In Fig. 3(a)-3(e), the photosensitivity spectral response *vs* wavelength curve for cadmium sulfide is plotted in the wavelength range of the maximum for several temperatures. At the lowest temperatures, there is only a slight indication of structure in the curve, but at 218°K and above, the presence of two components,

TABLE I. Dependence of band gap (photosensitivity maximum) on temperature between 90° and 400°K.

<i>Cadmium sulfide</i>	
$E=2.57-0.00052T$ ev	and $E=2.59-0.00052T$ ev
$\lambda=4807+1.10T$ A	and $\lambda=4772+1.10T$ A
<i>Cadmium selenide</i>	
$E=1.84-0.00046T$ ev	and $E=1.85-0.00046T$ ev
$\lambda=6726+1.84T$ A	and $\lambda=6661+1.84T$ A
<i>Cadmium telluride</i>	
$E=1.52-0.00036T$ ev	
$\lambda=8110+2.23T$ A	
<i>Zinc selenide</i>	
$E=2.80-0.00072T$ ev	
$\lambda=4401+1.30T$ A	

separated by about 35 Å is clear. The separation between the two components, which amounts to about 0.017 ev, does not change detectably between 218° and 341°K.

Similar results for cadmium selenide given in Fig. 3(f)-3(j), show that structure in the curve is detectable over the whole range of temperatures used. The separation between the components is about 65 Å, apparently independent of temperature. In energy units, the separation is about 0.015 ev, very nearly

¹¹ C. C. Klick, Phys. Rev. **89**, 274 (1953).

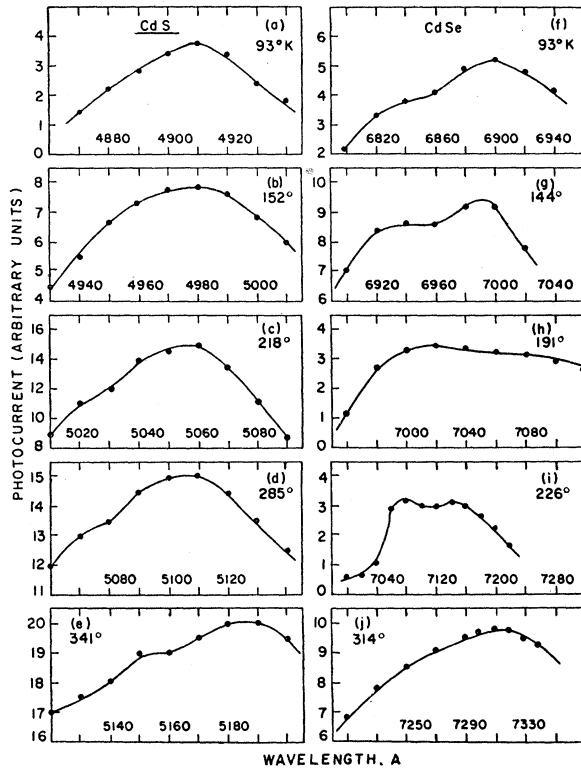


Fig. 3. The photocurrent (in arbitrary units) at the maximum of the photosensitivity *vs* wavelength curve for (a)–(e) cadmium sulfide, and (f)–(j) cadmium selenide, at several different temperatures.

the same as that found for cadmium sulfide. Both maxima have been plotted in Fig. 2 for cadmium selenide.

The relative magnitude of the two components for cadmium sulfide appears to be approximately independent of temperature. But for cadmium selenide, the low wavelength component increases in magnitude relative to the high wavelength component between 93° and about 200°K, and then decreases for temperatures between 200° and 314°K.

The existence of such structure in the photosensitivity maximum suggests the presence of double conduction or valence bands. No simple model of double bands seems able to describe adequately the experimental results. In particular, the temperature dependence of the relative magnitude of the two components for cadmium selenide seems to require an explanation involving more than optical transitions only.

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