

## New Pair Spectra in Gallium Phosphide

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Crystals of GaP doped with Zn+Te, Zn+Se, Cd+Te, and Cd+Se were grown from gallium-rich solutions contained in pyrolytic boron nitride crucibles, using vapor-grown GaP as source material. The low-temperature photoluminescence of these crystals reveals the presence of new pair spectra involving zinc or cadmium on gallium sites and tellurium or selenium on phosphorus sites (type II spectra). The values of  $(E_A + E_D)$ , the sum of the acceptor and donor binding energies, derived from the spectra are in excellent agreement with the values predicted from previously observed pair spectra. The data on all the previously observed spectra have also been recalculated to yield more consistent values of  $(E_A + E_D)$  and the Van der Waals parameter.

### INTRODUCTION

THE low-temperature photoluminescence spectra of certain GaP crystals grown from gallium solution contain a large number of emission lines which have been shown to arise from the recombination of holes and electrons trapped on distant donor-acceptor pairs.<sup>1</sup> In addition, the so-called "edge" emission has been shown to arise from the same type of radiative recombination.<sup>2</sup> To date, five types of pair spectra have been observed involving the postulated donor-acceptor pairs  $\text{Si}_P\text{S}_P(\text{I}_A)$ ,  $\text{Si}_P\text{Te}_P(\text{I}_B)$ ,  $\text{Si}_P\text{Se}_P(\text{I}_C)$ ,  $\text{Zn}_{\text{Ga}}\text{S}_P(\text{II}_A)$ , and  $\text{Cd}_{\text{Ga}}\text{S}_P(\text{II}_B)$  where the subscripts refer to the lattice sites occupied by the impurities and the spectral types (in parentheses) correspond to the notation used in Ref. 2. (I refers to an arrangement in which the donors and acceptors are on the same type of lattice sites, II refers to the arrangement on opposite lattice sites.) The purpose of this paper is to report the observation of new type II pair spectra involving the pairs  $\text{Zn}_{\text{Ga}}\text{Te}_P(\text{II}_C)$ ,  $\text{Zn}_{\text{Ga}}\text{Se}_P(\text{II}_D)$ ,  $\text{Cd}_{\text{Ga}}\text{Te}_P(\text{II}_E)$ , and  $\text{Cd}_{\text{Ga}}\text{Se}_P(\text{II}_F)$ . In addition, the data on the previously observed pair spectra have been recalculated to obtain a more consistent set of values for the parameters involved in determining the energies of the pair lines.

### EXPERIMENTAL

As discussed earlier,<sup>2</sup> our first attempts to obtain new spectral types were unsuccessful owing to the high background levels of silicon and sulfur and the resulting interference of the spectra involving the pairs Si-S, Si-Te, Zn-S, etc. The present crystals were grown by slowly cooling ( $5^\circ/\text{h}$ ) from  $\sim 1050^\circ\text{C}$  saturated solutions of GaP in gallium doped with 0.002 at.% zinc or 1% Cd and 0.0002% Se or 0.005% Te. The melts were contained in pyrolytic boron nitride crucibles (obtained from High Temperature Materials, Inc.) sealed under vacuum in vitreous silica tubes. The gallium was Alcoa 99.9999% material while the GaP source material was vapor grown GaP prepared from the elements by C. J.

Frosch using a wet hydrogen transport technique.<sup>3</sup> The vapor-grown GaP and pyrolytic boron nitride are thought to contain appreciably less sulfur and silicon, respectively, than the materials used previously. The photoluminescence measurements were performed as described in Ref. 2.

### RESULTS AND DISCUSSION

The new photoluminescence spectra at  $1.6^\circ\text{K}$  are shown in Figs. 1 and 2 where the numbers designate the assigned "shell number"  $m$  for the individual pair lines. The "shell number" is a convenient way of labeling the shells of atoms surrounding a central atom. Thus the nearest Se neighbors (on P sites) to a Zn atom (on a Ga site) will fall on the first shell; the next nearest, on the second shell, and so on, for the Zn-Se type II arrangement. For type II spectra  $m$  is related to the pair separation  $r$  by the relation  $r = (m/2 - 5/16)^{1/2}a_0$ , where  $a_0$  is the lattice constant of GaP taken to be 5.45 Å. For the type II arrangement, atoms occur at shells corresponding to all integral  $m$  values. This is not true of the type I arrangement for which certain  $m$  values have no atoms present, and gaps appear in the spectra.

Although the silicon and sulfur contamination has been reduced sufficiently to permit the observation of the new pair spectra, there is still a significant amount of contamination as shown by the presence of pair lines (designated by arrows) arising from other spectral types. Because of the improved control of the crystal doping, much more fine structure is discernible than was observed previously in the type II spectra. The fine structure splittings are largest for the Zn-Te spectrum. Interference by the extraneous pair spectra hinder the positive assignment of line splitting in some cases, and still more chemical purification is necessary to obtain "cleaner" spectra by reducing impurity contamination.

The validity of the assignments of the shell numbers is illustrated in Fig. 3 where the relative intensities of the Zn-Se pair lines are compared with values of  $N(r)$ , the number of pairs with a separation  $r$  for the corresponding shell number. The obviously good agreement be-

<sup>1</sup> J. J. Hopfield, D. G. Thomas, and M. Gershenson, *Phys. Rev. Letters* **10**, 162 (1963).

<sup>2</sup> D. G. Thomas, M. Gershenson, and F. A. Trumbore, *Phys. Rev.* **133**, A269 (1964).

<sup>3</sup> C. J. Frosch, *J. Electrochem. Soc.* **111**, 180 (1964).

tween the theory and experiment indicates that the assignments are correct.

The energies of the pair lines are plotted in Fig. 4 as a function of the pair separation  $r$  for the Zn-Se and Cd-Se spectra. The photon energy  $E(r)$ , corresponding to a specific pair, may be written

$$E(r) = E_{\text{gap}} - (E_A + E_D) + (e^2/\epsilon r) - (e^2/\epsilon)(\alpha^5/r^6), \quad (2)$$

at distances sufficiently large that additional terms are negligible.<sup>4,5</sup> Here  $E_{\text{gap}}$  is the energy gap,  $E_A$  and  $E_D$  are the acceptor and donor binding energies,  $e$  is the elec-

tronic charge,  $\epsilon$  is the low frequency dielectric constant, and  $\alpha$  is an adjustable Van der Waals parameter. In Refs. 1 and 2 Eq. (2) was erroneously written with the Van der Waals term involving  $(\alpha^6/r^6)$ , and some of the  $\alpha$  values were slightly in error. The data in Fig. 4 were fit by the use of a computer to Eq. (2) at large separations to obtain the best values of  $[E_{\text{gap}} - (E_A + E_D)]$  and of  $\alpha$ , as described in Ref. 2 and the dashed curves show the fit to this equation. Similar fits are obtained for the other spectral types. The values of  $[E_{\text{gap}} - (E_A + E_D)]$ , and  $\alpha$  and the derived values of  $(E_A + E_D)$

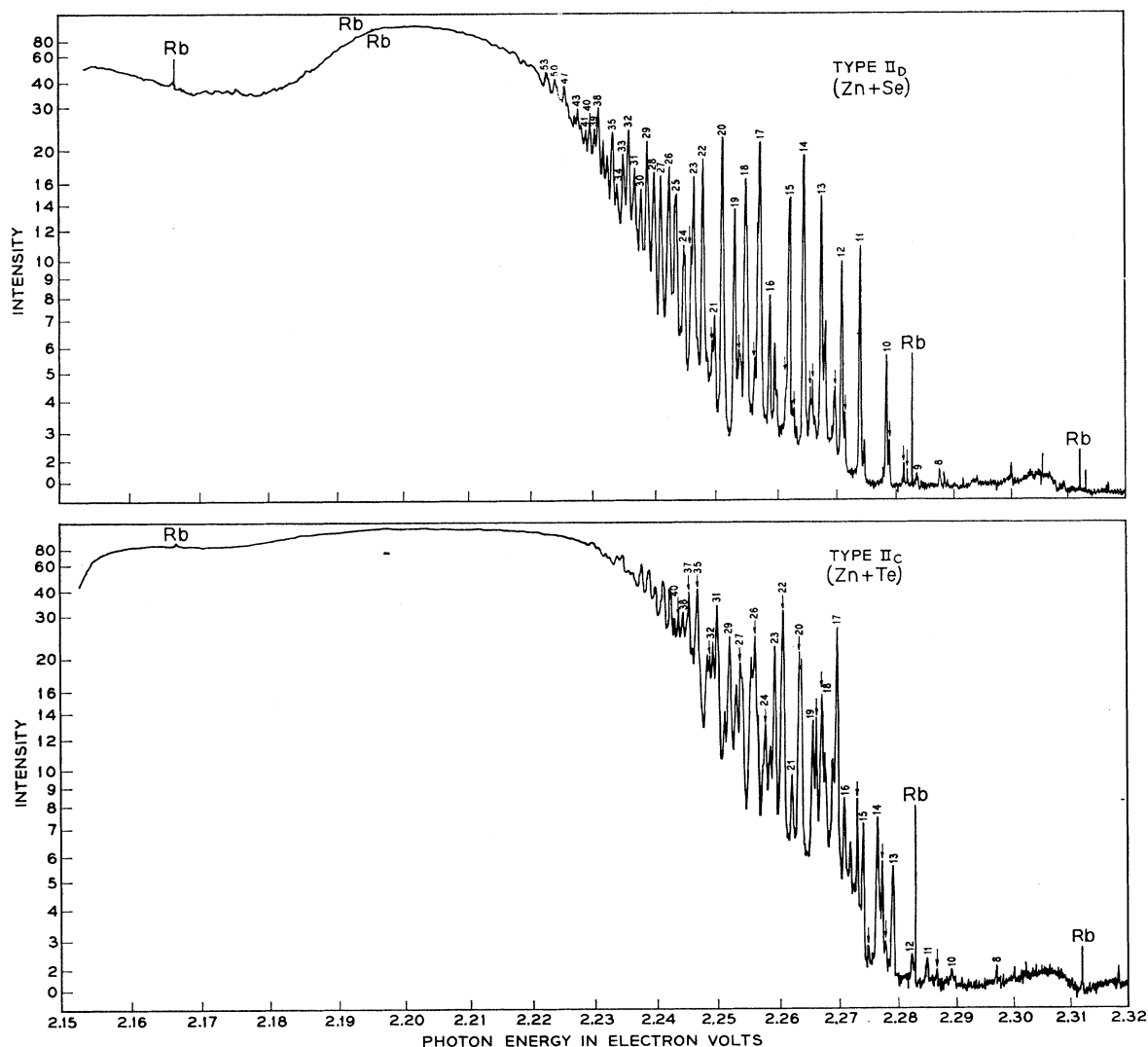


FIG. 1. Densitometer tracings from photographic plates of the photoluminescent spectra at 1.6°K of type II<sub>C</sub> and II<sub>D</sub> crystals produced by adding Zn+Te and Zn+Se, respectively. The intensities are on an arbitrary, nonlinear scale. The numbers correspond to the shell numbers of the pair lines of the corresponding pair spectra. The arrows designate the stronger extraneous pair lines due to other spectra (II<sub>A</sub> and I<sub>C</sub> for the type II<sub>D</sub>, and mainly II<sub>A</sub> for the type II<sub>C</sub> spectra). In some cases the extraneous lines are believed to overlap lines of the new spectral types so that the fine structure is obscured. In addition, more detail is evident on the original tracings than in these drawings. The lines marked Rb are rubidium calibration lines.

<sup>4</sup> F. E. Williams, Phys. Chem. Solids 12, 265 (1960).

<sup>5</sup> W. Hoogenstraaten, Philips Res. Rept. 13, 515 (1958).

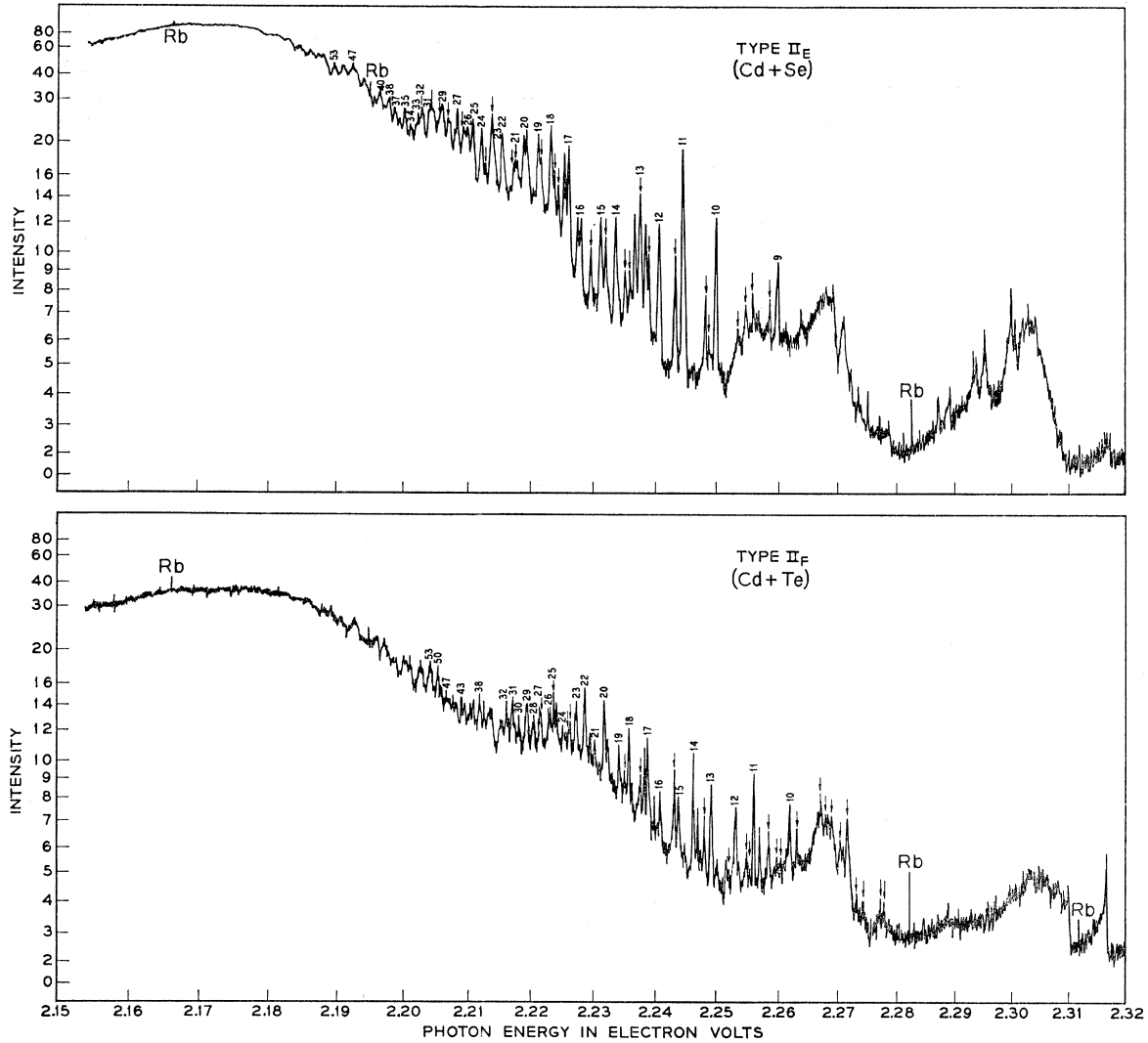


Fig. 2. Densitometer tracings from photographic plates of the photoluminescent spectra of type II<sub>E</sub> and II<sub>F</sub> crystals produced by the addition of Cd+Se and Cd+Te, respectively. The extraneous pair lines are II<sub>B</sub> and I<sub>B</sub> lines in the type II<sub>F</sub> and II<sub>B</sub> lines in the type II<sub>E</sub> spectra.

are summarized in Table I, together with the values for the previously observed pair spectra. The latter have been recalculated using in some cases new sharper

spectra to obtain more precise results. As before, the value of  $E_{\text{gap}}$  has been taken to be  $2.325 \pm 0.005$  eV. The consistency and precision of the data are illustrated by

TABLE I. Summary of parameters obtained by fitting spectral data to Eq. (2).

Spectral type and impurities	$E_{\text{gap}} - (E_A + E_D)$ (eV)	$(E_A + E_D)$ (eV)	$(E_A + E_D)$ predicted	$\alpha$ ( $\text{\AA}$ )	Position of broad peak (eV)	calc. $r$ for pair at peak ( $\text{\AA}$ )
	$\pm 0.002$	$\pm 0.007$				
I <sub>A</sub> (Si <sub>P</sub> Se <sub>P</sub> )	2.1856	0.1394	...	11.8	2.213	53
I <sub>C</sub> (Si <sub>P</sub> Te <sub>P</sub> )	2.1867	0.1383	...	10.7	2.213	55
I <sub>B</sub> (Si <sub>P</sub> Te <sub>P</sub> )	2.2007	0.1243	...	13.4	2.226	57
II <sub>A</sub> (Zn <sub>Ga</sub> Se <sub>P</sub> )	2.1701	0.1549	...	11.6	2.200	47
II <sub>D</sub> (Zn <sub>Ga</sub> Se <sub>P</sub> )	2.1718	0.1532	0.1538	11.7	2.202	47
II <sub>C</sub> (Zn <sub>Ga</sub> Te <sub>P</sub> )	2.1848	0.1402	0.1398	11.2	2.215	47
II <sub>B</sub> (Cd <sub>Ga</sub> Se <sub>P</sub> )	2.1369	0.1881	...	9.6	2.167	47
II <sub>E</sub> (Cd <sub>Ga</sub> Se <sub>P</sub> )	2.1383	0.1867	0.1870	9.5	...	...
II <sub>F</sub> (Cd <sub>Ga</sub> Te <sub>P</sub> )	2.1517	0.1733	0.1730	9.3	...	...

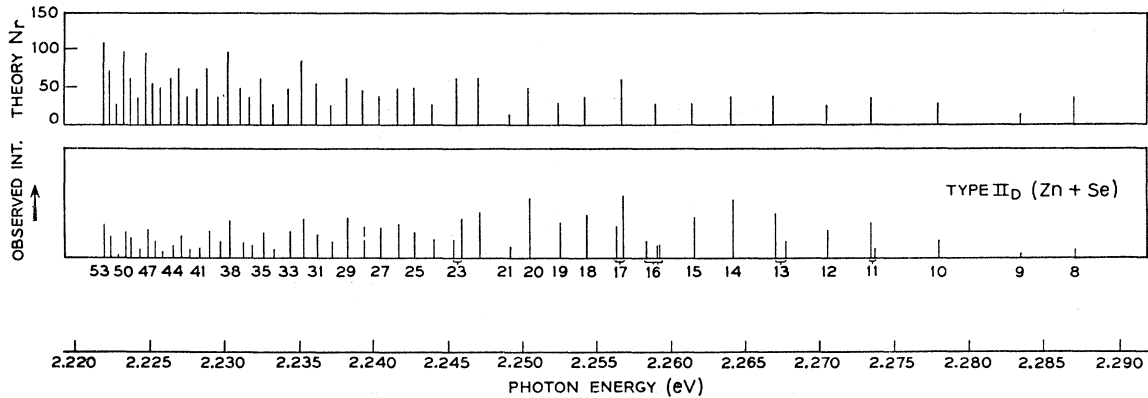


FIG. 3. The match between the values of  $N(r)$  and the observed intensities of the pair lines for type II<sub>D</sub> crystals at 1.6°K. The data were taken from photographic plates after subtraction of the broad background fluorescence. The positions of the  $N(r)$  values have been matched with the energies of the corresponding lines. In this plot a number of questionable lines which would add to the fine structure have been omitted (see Fig. 1). Inclusion of these lines would not appreciably alter the match between the  $N(r)$  and observed intensity patterns.

the fact that the changes in  $(E_A + E_D)$  in going from sulfur to selenium and sulfur to tellurium are seen to be the same; i.e.,  $0.0014 \pm 0.0003$  eV and  $0.0149 \pm 0.0002$  eV, respectively, for the type I and type II spectra involving the three different acceptor elements. Alternatively, the  $(E_A + E_D)$  values of all four of the new spectra described in this paper may be predicted from the  $(E_A + E_D)$  values of the old spectra. A comparison of the predicted and observed values is given in Table I. The agreement is seen to be good.

Also summarized in Table I are the positions of the broad peaks, under excitation intensities sufficient to produce the sharp pair lines, for most of the spectral

types and the calculated values of  $r$  for pairs radiating at these peak energies. (Because of interference by other pair spectra, the positions of the broad peaks for the Cd-Se and Cd-Te spectra could not be determined reliably.) It is seen that the calculated values of  $r$  are about 50 Å for all the spectra, supporting the previous conclusion that the broad emission and pair lines are intimately connected.

#### CONCLUSION

The experiments reported here obviously suggest that the attainment of many more pair spectra should be possible. Of particular interest would be very accurate Hall-effect measurements of the binding energies for at least two of the involved impurities in order to determine whether or not there is an equality between the optical and thermal binding energies of the impurities and, if there is, to obtain a more precise value of  $E_{gap}$ . If agreement were to be found between the optical and thermal values, pair spectra would provide a very convenient method of determining accurate binding energies since small, inhomogeneously doped crystals are quite adequate to provide very accurate data.

#### ACKNOWLEDGMENTS

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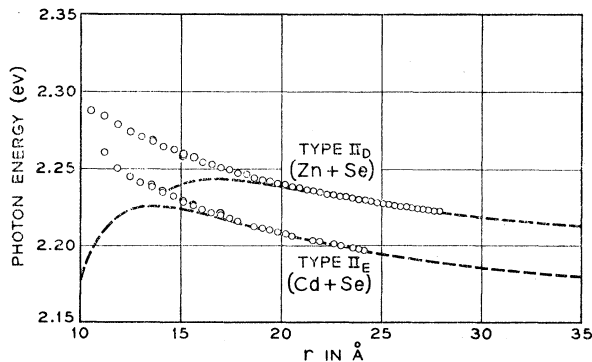


FIG. 4. The fit of the type II<sub>D</sub> and II<sub>E</sub> spectra to Eq. (2). The  $[E_{gap} - (E_A + E_D)]$  and  $\alpha$  values used to calculate the dashed lines are given in Table I.