

## Pair Spectra and "Edge" Emission in Gallium Phosphide

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The photoluminescence of GaP crystals grown from gallium solution has been observed at 20°K and below. The spectra contain many sharp lines. Some of these lines arise from excitons bound to point defects, but most are caused by the radiative recombination of electrons and holes trapped at donors and acceptors. The many lines arise from the many possible separations between the donors and acceptors. Five different types of spectra have been observed as a result of doping the crystals. The spectra may be analyzed to give the type of geometrical arrangement of donors and acceptors, and any particular line may be assigned to a particular pair separation. Considerable information may be deduced about the chemical centers involved; thus, the "pure" crystals are believed to contain S-Si pairs which are responsible for the fluorescence. Other pair spectra identified involve Te-Si, Se-Si, Zn-S, and Cd-S pairs. A great deal of the fluorescence occurs as broad emission. This so-called "edge" emission is observed to change with the line spectra as different impurities are incorporated in the crystals. Consequently, the broad emission is ascribed to recombination occurring at widely separated, nonisolated pairs. This conclusion is supported by observations of the change of the fluorescence with exciting intensity, and of the time decay of the fluorescence.

### I. INTRODUCTION

THIS paper gives an account of the radiative recombination in GaP of holes and electrons trapped at acceptors and donors. Although the experiments were performed at 20°K and below, the results are believed to be relevant to recombination occurring at higher temperatures, and also to other semiconductors. Hitherto it has been comparatively easy to interpret that portion of the fluorescence of semiconductors which consists of sharp line emission (and associated phonon effects) in terms of the decay of an exciton trapped at a point defect in the lattice. Such emission has been seen in GaP.<sup>1</sup> However, in GaP and in many other semiconductors, there is often an additional powerful broad emission near the band gap energy, the so-called "edge" emission, which has been more difficult to understand. Frequently, it is ascribed to the recombination of a free particle with a particle of the opposite sign trapped at an impurity center. Several objections can be raised to this contention, not least of which is its inability to explain the large, and essentially temperature-independent, half-width of the fluorescent bands.

In addition, GaP may display many sharp lines in fluorescence which have been recently shown to be associated with the recombination of a hole and an electron trapped at isolated donor-acceptor pairs with different discrete internuclear separations.<sup>2</sup> Two spectra, termed types I and II (designated as types I<sub>A</sub> and II<sub>A</sub> in this paper) were found, corresponding to recombination involving donors and acceptors on the same and on opposite lattice sites, respectively. In this paper several new such spectra are described which involve different donors and acceptors. It is clear that the broad emission, which is simultaneously present, is closely associated with the pair spectra, and indeed has its origin in the same type of phenomenon. The suggestion that recom-

bination occurs at donor-acceptor pairs is not new; it has been used to explain certain fluorescent phenomena in ZnS and related compounds<sup>3</sup> and theoretical treatments of the process have been given.<sup>4</sup> However, the evidence for such pair effects has been rather indirect and it has usually been considered that closely spaced pairs have been of primary importance. In GaP the line spectra provide convincing evidence of the pair effects and show that emission may result from recombination occurring between holes and electrons trapped at centers separated by 50 Å or more.

### II. EXPERIMENTAL

#### A. Growth of Crystals

Most of the crystals were grown by slowly cooling gallium-rich solutions.<sup>5</sup> Sealed evacuated vitreous silica tubes containing the Ga-GaP-dopant mixtures were heated to temperatures between 1000 and 1275°C and then program cooled at rates of 3 to 5°/h down to about 200 or 300°C below the initial growth temperature. The samples were then either removed from the furnace or cooled in the furnace to near room temperature. In a few experiments cooling was accomplished by using a vertical Bridgman technique.<sup>6</sup> The melts contained between 5 and 50 g of gallium, the desired amount of dopant, and enough GaP to saturate the gallium at the initial growth temperature. The larger melts were necessary in order to obtain a reasonable degree of accuracy in weighing extremely small percentages of the dopant (sometimes ~5 μg) and/or to

<sup>3</sup> E. F. Apple and F. E. Williams, *J. Electrochem. Soc.* **106**, 224 (1959); J. S. Prener and F. E. Williams, *Phys. Rev.* **101**, 1427 (1956).

<sup>4</sup> F. E. Williams, *J. Phys. Chem. Solids* **12**, 265 (1960); W. Hoogenstraaten, *Philips Res. Rept.* **13**, 515 (1958).

<sup>5</sup> See, for example, J. F. Miller, in *Compound Semiconductors. Vol. I. Preparation of III-V Compounds*, edited by R. K. Willardson and H. L. Goering (Reinhold Publishing Corporation, New York, 1962), Chap. 23.

<sup>6</sup> See, for example, J. Starkiewicz and J. W. Allen, *J. Phys. Chem. Solids* **23**, 881 (1962).

<sup>1</sup> D. G. Thomas, M. Gershenzon, and J. J. Hopfield, *Phys. Rev.* **131**, 2397 (1963).

<sup>2</sup> J. J. Hopfield, D. G. Thomas, and M. Gershenzon, *Phys. Rev. Letters* **10**, 162 (1963).

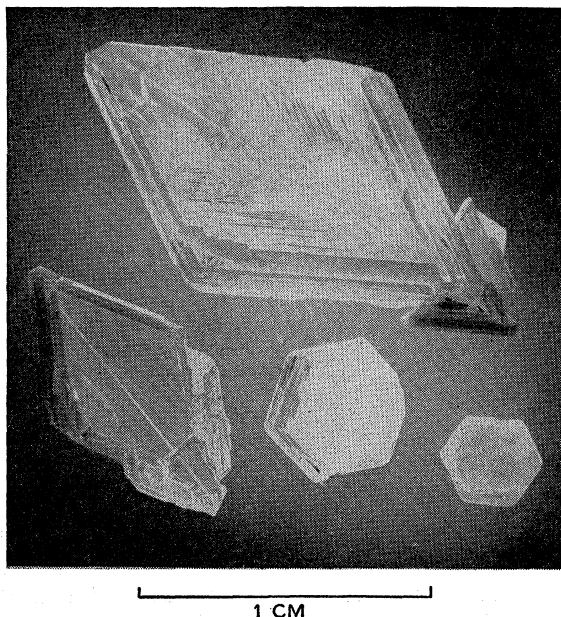


FIG. 1. Some typical crystals of GaP grown from Ga solution using the slow-cooling technique.

obtain sufficiently large crystals at the lower initial growth temperatures where the GaP solubilities are relatively small.<sup>7</sup> In some experiments the melts were contained in AlN, BN or Al<sub>2</sub>O<sub>3</sub> crucibles which were in turn sealed in evacuated silica tubes. The GaP source material was either boat grown (in graphite) material obtained from the Merck Co. or from Derick and Frosch, floating zone material from Derick or vapor grown material from Frosch. The gallium metal was 99.9999% pure material from Alcoa while the AlN, BN and Al<sub>2</sub>O<sub>3</sub> crucibles were the highest purity crucibles obtainable from the Alcoa, Carborundum, and Morganite Companies, respectively. The silica tubing was either Vitreosil from the Thermal American Fused Quartz Company or General Electric grade 204A.

The resulting crystals, recovered by dissolving away the gallium in conc. HCl, were predominately platelets with {111} major faces, one side rough and one side smooth, corresponding to the phosphorus and gallium faces, respectively.<sup>8</sup> Typical platelets are shown in Fig. 1. The samples were normally diamond shaped as seen in Fig. 1 with very few of the more perfect hexagonal platelets being found. The former type is a dendritic growth showing the features observed in the growth of III-V dendrites from the melt as discussed by a number of workers.<sup>9</sup> The diagonal lines seen in the two dendritic crystals consisted of channels of trapped gallium prior to digesting in HCl. In addition, there were often layers of occluded gallium parallel to the

major faces, probably formed by trapping of gallium between the H-arms formed in dendritic growth.<sup>9</sup> All this serves to indicate the structural inhomogeneity of most of these crystals in addition to the inherent nonuniformity due to the fact that growth occurs over a range of temperatures and melt compositions. As a result, variation in properties from crystal to crystal should not be surprising. However, the slow cooling technique is useful for preparing crystals relatively rapidly for the survey type of work described herein.

More uniform crystals may be prepared by using a sealed tube thermal gradient technique as described previously for the growth of germanium and silicon.<sup>10</sup> Some crystals were grown by using this method at temperatures between 780 and 1080°C. Vitreous silica tubes and, in some cases, BN crucibles contained in silica tubes were used.

#### Conditions for Producing Crystals Showing Spectral Lines

Approximately 300 samples have been prepared by using the two methods discussed above. A summary of the results most pertinent to the attainment of the various spectral types follows. Because of the extreme sensitivity of the intensities of the spectra to slight variations in impurity content and the lack of highly purified and well-defined GaP for source material, no significant correlations were found relating the fluorescence to method of growth, growth temperatures, cooling rate, and other crystal growth parameters. Therefore, these parameters will not be considered further. The values of  $(N_D - N_A)$  quoted below were obtained from surface barrier capacitance measurements.<sup>11,12</sup> The nonuniformity of the crystals is evident from the fact that for undoped crystals the smooth side would usually be *n* type, the opposite side *p* type. The fluorescence measurements and  $(N_D - N_A)$  data were taken on the smooth sides.

*Type I<sub>A</sub>.*<sup>13</sup> Bright, sharp type I<sub>A</sub> spectra were obtained almost invariably with crystals grown from undoped melts in silica. Significantly fainter spectra were usually obtained when the undoped melts were contained in Al<sub>2</sub>O<sub>3</sub>, BN, or AlN crucibles. When pieces of fused silica were added to melts contained in these crucibles, the type I<sub>A</sub> spectra were generally brighter than when silica was not added although there were some exceptions. The addition of small amounts of silicon or sulfur (~0.00001–0.01 at.%) to the melts in silica did not affect the spectral type although the fluorescence intensity decreased with increasing im-

<sup>9</sup> See, for example, O. Lindberg and J. W. Faust, Jr., in Ref. 5; Chap. 34.

<sup>10</sup> F. A. Trumbore, C. R. Isenberg, and E. M. Porbansky, *J. Phys. Chem. Solids* **9**, 60 (1959).

<sup>11</sup> H. G. White and R. A. Logan, *J. Appl. Phys.* **34**, 1990 (1963).

<sup>12</sup> R. A. Logan and H. G. White (private communication).

<sup>13</sup> The characteristics of the various spectral types are discussed in Section III.

<sup>7</sup> M. Rubenstein, *Electrochem. Soc., Spring Meeting*, Los Angeles, 1962 [Extended Abstracts **11**, 129 (1962)]; R. N. Hall, *J. Electrochem. Soc.* **110**, 385 (1963).

<sup>8</sup> E. H. Turner (private communication).

purity content until at higher doping levels the luminescence disappeared. This decrease in intensity at higher doping levels was also found for the other spectral types discussed below. Although there was a tendency for the brighter samples to be associated with low  $(N_D - N_A)$  values ( $\sim 10^{15} - 10^{17} \text{ cm}^{-3}$ ), good type I<sub>A</sub> spectra have been obtained with  $(N_D - N_A)$  values as high as  $\sim 5 \times 10^{18} \text{ cm}^{-3}$ . It might be noted that melts containing a few at. % silver, gold, iron, cobalt, nickel, or vanadium also yielded good type I<sub>A</sub> crystals with  $(N_D - N_A)$  values of  $\sim 10^{17} - 10^{18} \text{ cm}^{-3}$ .

*Types I<sub>B</sub> and I<sub>C</sub>.* Types I<sub>B</sub> and I<sub>C</sub> spectra were observed for crystals grown from melts containing  $\sim 0.01 - 0.1$  at. % tellurium and  $\sim 0.00002 - 0.0001$  at. % selenium, respectively. As the concentrations were lowered below the values quoted, the types I<sub>B</sub> or I<sub>C</sub> spectra disappeared with type I<sub>A</sub> spectra increasing in intensity. The measured values of  $(N_D - N_A)$  for the fluorescing crystals were generally  $\sim 1 - 5 \times 10^{18} \text{ cm}^{-3}$ .

*Types II<sub>A</sub> and II<sub>B</sub>.* When zinc was added to melts in concentrations between  $\sim 0.01$  and  $0.3$  at. %, type II<sub>A</sub> spectra were observed. The intensities were in general appreciably stronger than for types I<sub>B</sub> and I<sub>C</sub> and were comparable to the intensities of the best type I<sub>A</sub> crystals.  $(N_A - N_D)$  values of  $\sim 10^{16} - 10^{18} \text{ cm}^{-3}$  were measured on the fluorescent crystals.

It is necessary to add between about 5 and 20 at. % cadmium to the melt before obtaining type II<sub>B</sub> spectra which were slightly less bright than the best type I<sub>A</sub> or II<sub>A</sub> crystals. Type I<sub>A</sub> spectra were present to at least a slight extent in both type II<sub>A</sub> and II<sub>B</sub> crystals. The fact that only at 20 at. % cadmium in the melt were *p*-type crystals obtained suggests that the distribution coefficient of cadmium in GaP is quite low, just as the distribution coefficient of selenium must be quite high. More extensive data on distribution coefficients of the pertinent impurities will be discussed elsewhere.<sup>14</sup>

*Type O.* The first crystals showing type-O spectra were obtained when two silica tubes containing  $\sim 0.5$  mole % Ga<sub>2</sub>O<sub>3</sub> and  $\sim 1$  mole % NaCl were heated above  $\sim 1200 - 1250^\circ\text{C}$ . The combined partial pressures of phosphorus and Ga<sub>2</sub>O or NaCl apparently exceeded 1 atm and blew out the top of the softened silica tubes, exposing the melts to the atmosphere. The  $(N_D - N_A)$  values were  $\sim 5 \times 10^{17} \text{ cm}^{-3}$  for these crystals. When the same experiments were carried out at  $\sim 1125^\circ\text{C}$ , the tubes did not explode and type I<sub>A</sub> spectra were obtained for both samples although there was an indication of type-O lines in the crystals from the Ga<sub>2</sub>O<sub>3</sub> doped melts. A number of experiments were carried out with sealed tubes containing partial pressures of air or water vapor, with tubes open to the atmosphere or open to air and H<sub>2</sub>O vapor. Also there were a number of other runs where accidental cracking or explosion occurred. While

the most probable correlation involves the presence of oxygen, some crystals in contact with Ga<sub>2</sub>O<sub>3</sub> or oxygen did not show type-O spectra. The work of Woods and Ainslie<sup>15</sup> on the reduction of the silicon content of GaAs in the presence of oxygen may be pertinent here.<sup>16</sup>

#### Attempts to Obtain Other Spectral Types

Attempts were made to obtain other type-II spectra by doping with combinations such as Zn+Te, Cd+Te, Zn+Se, etc. Despite efforts to vary combined doping levels over very wide ranges, only the types described above have been observed. Attempts to obtain type II spectra by adding magnesium in crucibles other than silica have only yielded type-I<sub>A</sub> spectra, possibly due to reaction with the silica impurity in the AlN, BN, or Al<sub>2</sub>O<sub>3</sub> crucibles. Attempts to obtain variations of the type I spectra by adding germanium, tin or lead have also thus far produced only type I<sub>A</sub> spectra. The problem thus seems to be to eliminate the silicon and/or sulfur contamination. Use of the temperature gradient zone melting technique<sup>17</sup> might overcome the silica problem.

#### B. Apparatus

The lines described in this paper cannot be seen in absorption in crystals currently available, but they are observed in fluorescence. The fluorescence has usually been stimulated by focusing two HBO 200 high-pressure Hg lamps onto the crystal using two *f*/1.5 quartz lenses. The exciting light was filtered by 7-59 Corning filters so that the strongly absorbed wavelengths shorter than about 4800 Å were used. The crystals were immersed in liquid hydrogen or helium in a glass Dewar. The spectra were usually recorded photographically using a *f*/17 spectrograph giving a dispersion of 2 Å/mm. Direct recording with a photomultiplier was also possible and was sometimes useful. Microphotometer recordings of the plates were made and from these the energies of the lines were obtained with the help of an electronic computer. The computer was also used to fit the data to the theoretical formula mentioned below. Since the doped crystals were noted to be somewhat inhomogeneous, those sections of the crystal which gave the clearest lines were focused on the entrance slit of the spectrograph.

<sup>15</sup> J. F. Woods and N. G. Ainslie, *J. Appl. Phys.* **34**, 1469 (1963).

<sup>16</sup> The outgassing treatment prior to sealing off the silica tubes may affect the amount of oxygen and (or) silicon in the melt. Starkiewicz and Allen (Ref. 6) carried out a relatively thorough outgassing procedure, heating the tube containing gallium and GaP up to the softening point of the silica under vacuum. We tried a similar experiment involving an undoped melt and found not only little fluorescence but also a relatively high doping level. We believe this to be due to Si contamination, although the possibility that compensating sulfur impurity is being vaporized should be considered.

<sup>17</sup> W. G. Pfann, *J. Metals* **7**, 961 (1955); A. I. Mlavsky and M. Weinstein, *J. Appl. Phys.* **34**, 2885 (1963).

<sup>14</sup> F. A. Trumbore, M. Kowalchik, H. G. White, C. L. Luke, and R. L. Barns, *Electrochem. Soc. Meeting*, New York, Sept. 29-Oct. 3 (1963), *Extended Abstracts of Electronics Division*, **12**, No. 2, p. 60.

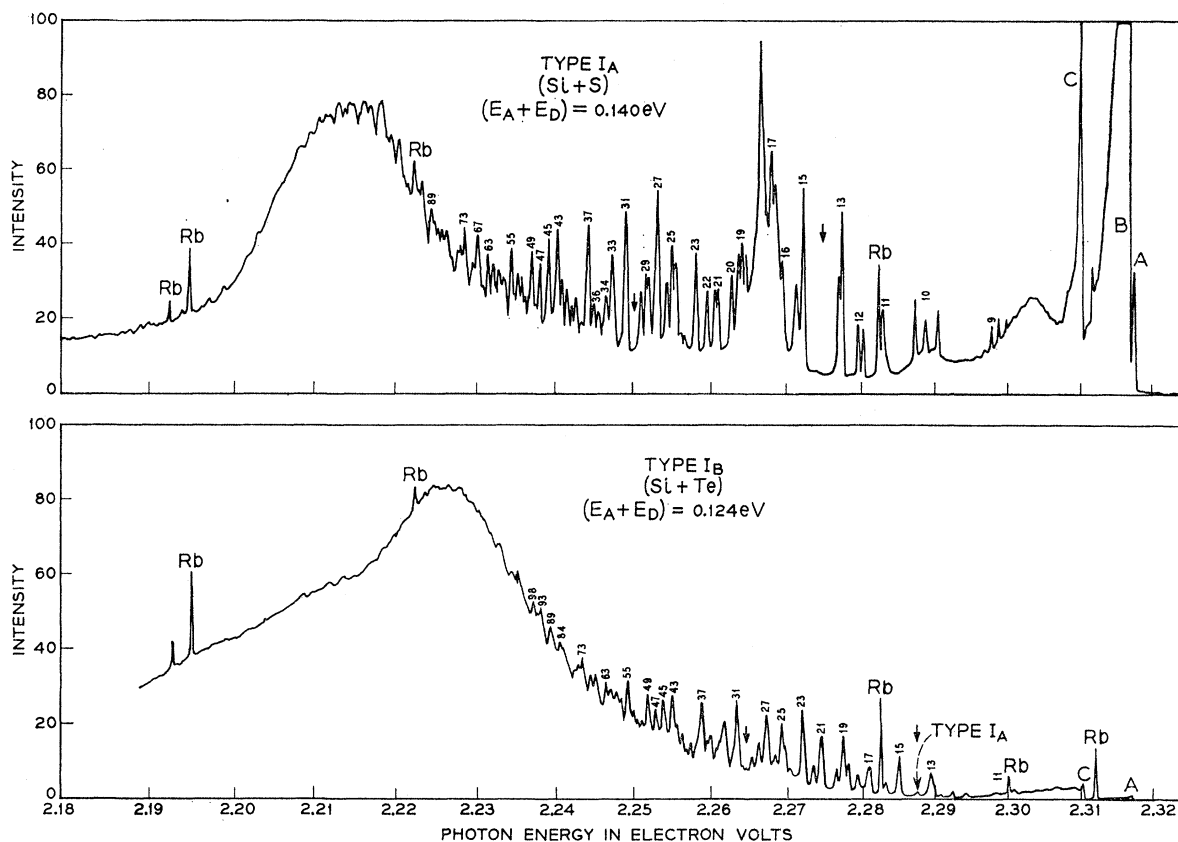


FIG. 2. The photoluminescent spectra (on arbitrary scales) of type  $I_A$  and  $I_B$  crystals taken at  $1.6^\circ\text{K}$ . The lines marked Rb are rubidium calibration lines. The small numbers indicate the shell numbers of the pair spectra. A, B, and C are bound exciton lines. The arrows indicate some positions for which  $N(r)=0$ , and mark a gap in the spectra. The type  $I_A$  crystals are grown without the addition of impurities; the  $I_B$  crystals are produced by adding Te.

### III. RESULTS AND DISCUSSION

#### A. Observed Spectra

Most of the undoped crystals give what will be called type  $I_A$  fluorescent spectra. This is illustrated in Fig. 2 which shows such a spectrum taken at  $1.6^\circ\text{K}$ . (The nomenclature differs from that of Ref. 2; the generic types are now defined as I and II, the particular spectra being designated as  $I_A$ ,  $I_B$ , etc.) There are certain lines, A, B, C, etc., and phonon replicas of some of these lines, which are connected with point defects and are quite unrelated to the pair lines. These lines occur without the pair lines in type O crystals. Why this is so is not at present clear. The nature of these point defect lines, which are usually much weaker in doped crystals, has been discussed elsewhere.<sup>1</sup> The pair lines have been marked with their shell, or  $m$ , numbers as described below. It will be noticed that sometimes there are more than one line with the same  $m$  number—it may then be said that the spectrum shows fine structure.

The type  $I_C$  spectra, obtained with Se-doped crystals, are very similar to type  $I_A$  spectra except that the lines are all shifted about  $0.0016$  eV to higher energies. Faint type  $I_A$  lines are often interspersed among the new

lines but they can be readily identified by comparison with a normal type  $I_A$  crystal. The addition of tellurium produces a type  $I_B$  spectrum which is also illustrated in Fig. 2. Figure 3 shows the type  $II_A$  and  $II_B$  spectra produced by the addition of zinc and cadmium, respectively. (Particularly clear type  $I_A$  lines may be seen in the background of the  $II_B$  spectrum.)

At temperatures above  $1.6^\circ\text{K}$  (e.g.,  $4.2$  and  $20^\circ\text{K}$ ) the pair spectra became more complex due to the appearance of more lines interleaved among those present at  $1.6^\circ\text{K}$ . Since these additional lines serve only, at this stage, to complicate the situation they will not be further discussed.

Figures 2 and 3 show line spectra but they also show that much of the fluorescence is associated with broad bands falling at energies below the line spectra. These broad bands are repeated at a series of lower energies separated from the highest energy band by approximate multiples of the longitudinal optical-phonon energy.<sup>18</sup> This is illustrated in Fig. 4 for a type  $I_A$  crystal.

The emission from any particular crystal is strongly dependent on the conditions of excitation. As the ex-

<sup>18</sup> D. A. Kleinman and W. G. Spitzer, Phys. Rev. 118, 110 (1960).

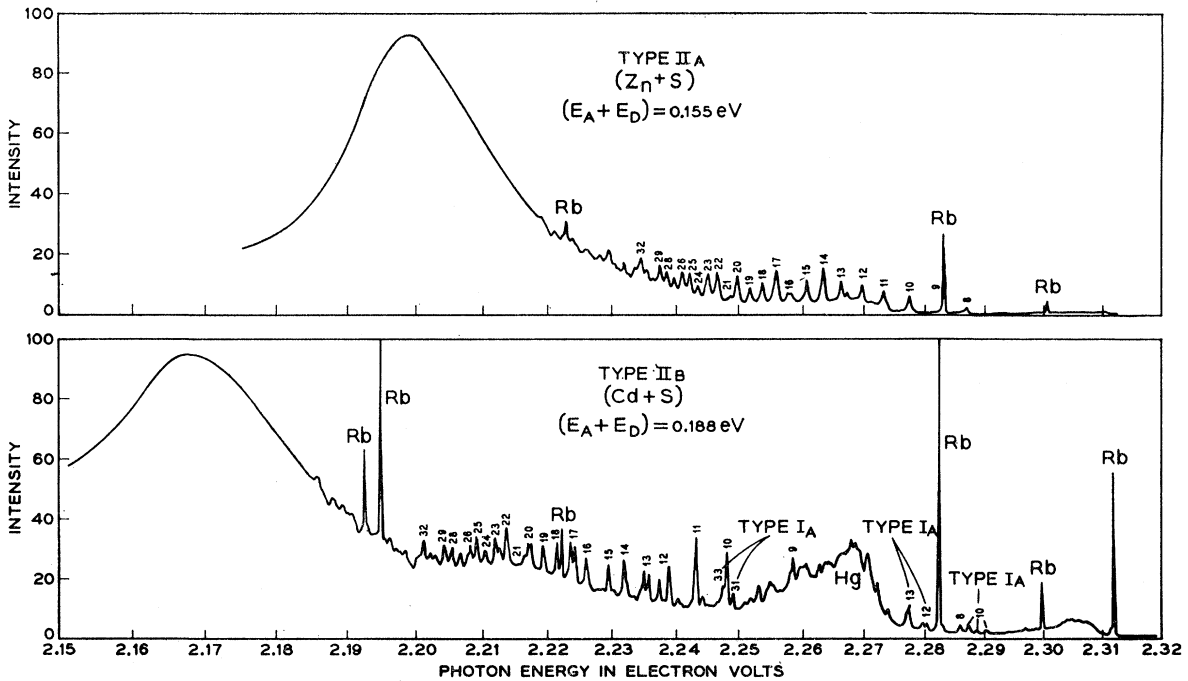


FIG. 3. The photoluminescent spectra (on arbitrary scales) at 1.6°K of type II<sub>A</sub> and II<sub>B</sub> crystals, produced by the addition of Zn and Cd, respectively. Some mercury light used for excitation appears in the rather weak fluorescence seen from II<sub>B</sub> crystals and has been labeled Hg. Numerous type I<sub>A</sub> lines are seen in the background of the II<sub>B</sub> spectrum.

citing intensity is reduced from the level used to produce the spectra of Figs. 2 and 3, the lines first become less intense and ultimately disappear. Next, the broad emission peak moves to lower energies, and at the same time becomes somewhat narrower. The shift of the peak is illustrated in Fig. 5 in which the position of the broad peak is plotted as a function of exciting intensity for a type I<sub>A</sub> crystal.

Another method of excitation is to focus an E. G. G. FX12 xenon discharge tube (filtered to pass only band gap radiation) onto the crystal, so that the crystal can be strongly excited for a few microseconds. The total emission from the crystal, which is often found to be spread over many seconds, is then photographed at the focal plane of the spectrograph. Many flashes are necessary to produce an exposure. The resulting spectra differ from the continuously excited spectra in the following ways: (a) The relative strengths of the bound exciton lines A, C, etc. are increased. (b) The pair spectra lines are absent or very weak. (c) The broad emission is present but shifted to long wavelengths, as though the sample were being excited by a very weak continuous source. Figure 6 which shows microphotometer traces of the same crystal with (a) intense dc excitation and (b) flash excitations illustrates these points.

**B. Interpretation of Lines as Pair Spectra**

The large number and regularity of the pair lines suggests that they have a different origin from that of

the bound exciton lines. The recombination of an electron trapped at a donor and a hole trapped at an acceptor will result in radiation at a frequency which will depend on the separation between the donor and acceptor. Since the impurities fall on lattice sites, the separations will be discrete and hence line spectra could result. This model is subject to quantitative checks.

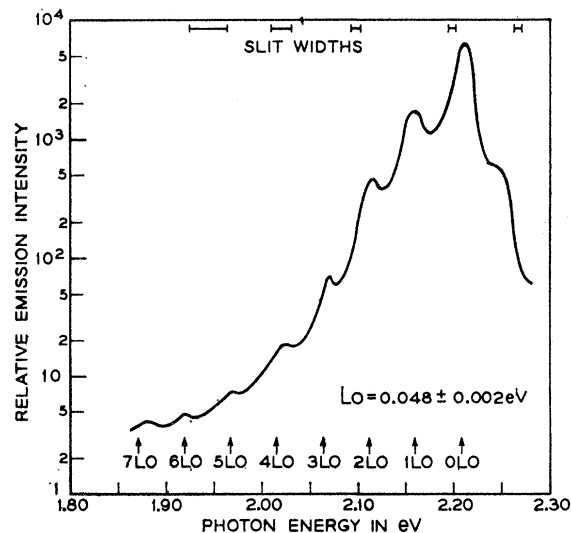


FIG. 4. The photoluminescence of a type I<sub>A</sub> crystal taken at 20°K showing the repetition of the main peak at lower energies due to phonon emission. The shoulder near 2.25 eV contains the unresolved pair lines.

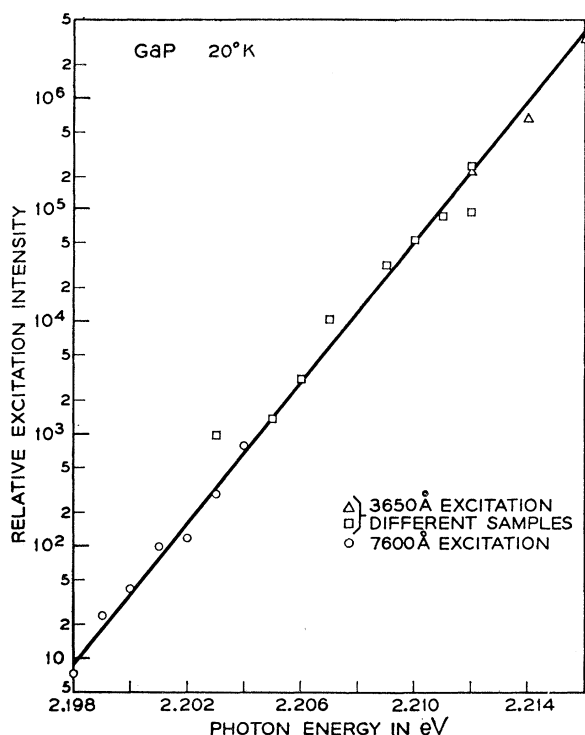


FIG. 5. The position of the broad peak of the photoluminescence of a type I<sub>A</sub> crystal at 20°K as a function of the excitation intensity. For the lowest levels of excitation it was necessary to use penetrating red light (7600 Å), which acted presumably by a two-step process. These points were joined smoothly onto the points obtained using nonpenetrating uv excitation.

By considering the energetics of bringing a hole and an electron from infinity to an ionized donor-acceptor pair with a separation,  $r$ , large compared to the diameter of the neutral donor and acceptor states, the energy of the state may be written

$$E(r) = E_{\text{gap}} - (E_A + E_D) + (e^2/\epsilon r), \quad (1)$$

where  $E(r)$  will be the energy of the fluorescent line,  $E_{\text{gap}}$  is the band gap of the semiconductor,  $E_A$  and  $E_D$  are the acceptor and donor binding energies,  $e$  is the electronic charge, and  $\epsilon$  is the low frequency dielectric constant. The low-frequency dielectric constant is the correct quantity to use here since we are considering the interaction of an electron, say, with a charge removed a large distance compared to the diameter of the bound electron state. At closer separations a Van der Waals attractive term may exist between the neutral donor and acceptor and Eq. (1) becomes

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

where  $a$  is an adjustable parameter. Clearly this additional term is somewhat empirical and it is quite possible that other long range forces such as strain, with different dependences on  $r$ , may be more important. If so, the extrapolations described below obtained with the aid of this equation may be in error by a few MeV.

Certainly the equation becomes inadequate at closer separations, where the additional terms described by Williams<sup>4</sup> may be relevant.

### C. The Identification of Lines with "Shell Numbers"

In order to test the  $E(r)$  relation it is necessary to decide  $r$  for any observed line. If the assumption of a random distribution of donors and acceptors is made, then it may reasonably be expected that over any small range of  $r$  the intensities of the lines will be approximately proportional to the statistical probability of a particular pair occurring. This is proportional to the number of possible combinations of sites which give the particular separation. This is readily calculable and is not a monotonically increasing function of  $r$ . Consequently, a characteristic intensity pattern might be sought which would identify the lines. A long-range correlation of the calculated and observed intensity patterns is not expected since matrix elements, capture cross sections, linewidths and other influences will vary with  $r$ .

Donors and acceptors in GaP may in principle occupy substitutional or interstitial sites. At substitutional sites two types of arrangements are possible, type I with both impurities on the same type of lattice site (i.e., both on phosphorus sites or both on gallium sites), and type II with the impurities on opposite sites. Atoms on interstitial sites (of which there are two kinds) may give type I and II arrangements, and in addition there is a type III array with one impurity at an interstitial site and one at a particular substitutional site. It may be noted that considerable simplifications result from having a cubic binary crystal. Thus, in germanium or silicon an indiscriminate mixture of type I and II lines will result from substitutional impurities, and in a noncubic crystal many additional lines will result from the angular dependence of  $r$  for a given shell and from the anisotropy in the dielectric constant.

An example of the calculation of  $N(r)$ , the number of pairs with a separation  $r$ , for the type I arrangement is given in the Appendix. The results of these calculations for the various "shell numbers"  $m$  are plotted for types

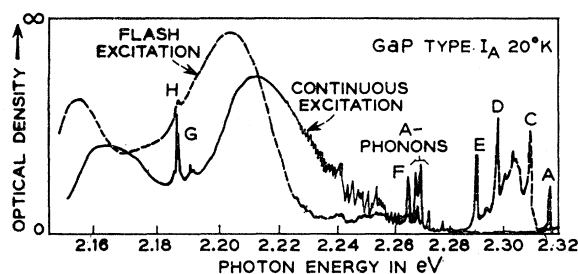


FIG. 6. The photoluminescence on a nonlinear scale of a type I<sub>A</sub> crystal under a different condition of excitation. Continuous excitation here produced the pair lines strongly and the bound excitons weakly, whereas the reverse is true for flash excitation. Notice also that the broad peak occurs at lower energies for flash excitation.

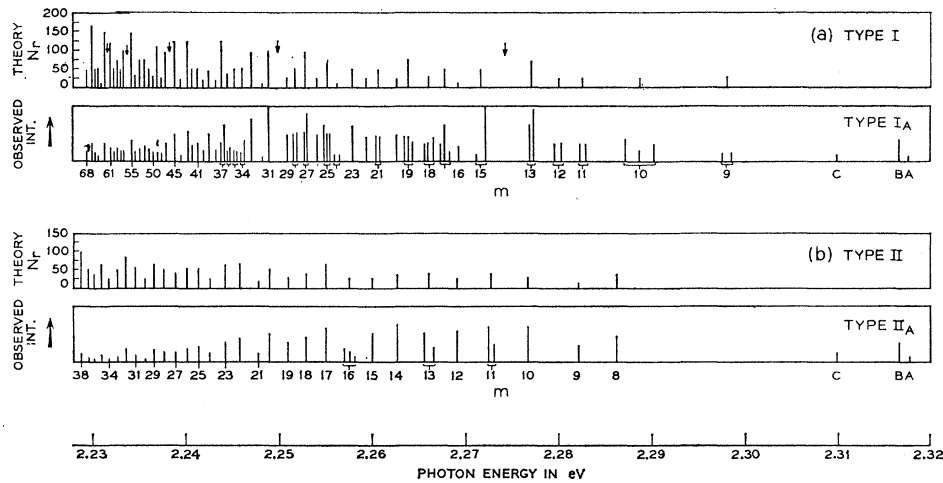


FIG. 7. The match between the  $N(r)$  values and the observed intensities of the pair lines for type  $I_A$  and  $II_A$  crystals at 1.6°K. The data have been taken from a photographic plate after the subtraction of broad background fluorescence. The positions of the  $N(r)$  values have been matched with the energies of the corresponding experimental lines.

I and II in the top sections of each part of Fig. 7. The shell number is a convenient way of labeling the shell, the first shell having  $m=1$ , and so forth. The separation  $r$  is a smooth function of  $m$ , and consequently the energy of the various lines may be expected also to be a smooth function of  $m$ . Values of  $r$  are,

$$r = (\frac{1}{2}m)^{\frac{1}{2}}a_0 \quad (\text{Type I})$$

and

$$r = (m/2 - 5/16)^{\frac{1}{2}}a_0 \quad (\text{Type II}),$$

where  $a_0$  is the lattice constant which is taken to be 5.45 Å.<sup>19</sup> It happens that for the type I geometry, there are certain  $m$  values which have no atoms at the corresponding  $r$  values. These are referred to as shells with  $N(r)=0$ , and may be expected to result in gaps in the spectra. No such shells occur for the type II geometry.

The observed spectra contain fine structure which does not help in the correlation of the lines with the  $N(r)$  values. Some of this fine structure can be eliminated by working at low temperatures. As noted above, there are more lines at 20 than at 4.2°K, and more at 4.2 than at 1.6°K, and it is possible to observe that the extra lines diminish in intensity as the temperature falls. Clearly the upper state of the pairs may be split into levels which become thermally populated. The causes of the splittings may include: (a) Splitting of the valence band as a result of the strain associated with the pair; (b) Spin-spin interactions between the hole and electron, which for excitons at least can result in splittings of the order of  $10^{-3}$  eV; (c) Valley orbit splitting of the electron since it is derived from a many-valley conduction band. The first two effects will become smaller the larger  $r$ , the last may be so large that the excited electron states are not at all involved at the temperatures used. (Once a spectrum has been identified,

it is, of course, quite possible to observe it at 20°K and from then on it may be identified at 20°K if this is convenient.)

Using the 1.6°K data it is not hard to find a unique fit between theory and experiment. This fit is illustrated for type  $I_A$  (undoped) crystals, and type  $II_A$  (Zn-doped) crystals in Fig. 7. However, even at 1.6°K the data exhibit fine structure which is not due to thermal population effects, and in the comparison with theory these lines must be lumped together. There is usually little ambiguity as to which lines belong to which  $m$  number. Of particular note are the gaps in the type  $I_A$  spectra at the shell numbers for which  $N(r)=0$ . These gaps are of course particularly useful for the identification of the  $m$  numbers. As expected, there is no agreement between the  $N(r)$  values and the observed intensities over a large range of  $r$ .

The fine structure shows that pairs with the same  $r$  value may emit at different energies even at the lowest temperatures. This inequivalence of pairs may arise from at least two circumstances:

(a) For certain  $m$  numbers there are two or more symmetrically inequivalent sets of sites. Consider the 13th shell of type I. If one atom is at (000), the other may be at a set of coordinates of the type (4,3,1), or of the type (5,1,0) (see Appendix). The wave functions of the bound holes and electrons are not expected to have spherical symmetry, so that the two sets of sites may well have different energies.

(b) In counting the number of possibilities for each set of sites the assumption has been made that the lattice of sites has a center of symmetry. For the lattices considered this is true, but for GaP itself it is not. Consequently some of the sets of pairs assumed to be equivalent will not be, and in reality the lines will be doubled. These two factors can account for the existence of most, if not all of the observed fine structure,

<sup>19</sup> G. Giesecke and H. Pfister, Acta. Cryst. 11, 369 (1958).

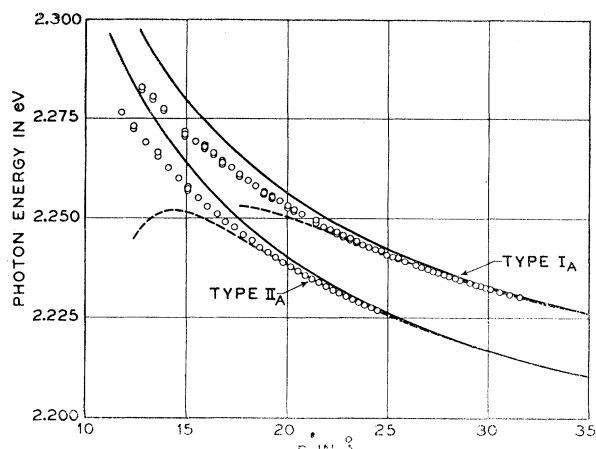


FIG. 8. The fit of the types  $I_A$  and  $II_A$  spectra to Eqs. (1) and (2). The solid lines exclude the Van der Waals term, the dashed include it. The  $[E_{\text{gap}} - (E_A + E_D)]$  and  $a$  values used to calculate the lines are given in Table I.

and this observation of the expected multiplicity for particular  $m$  values further confirms the assignment of the lines already made.

#### D. The Energies of the Lines

Since  $E(r)$  and  $r$  are now known for each of the lines, Eqs. (1) and (2) may be tested. For this purpose the room-temperature lattice constant,  $5.45 \text{ \AA}$ ,<sup>19</sup> and dielectric constant,  $10.18$ ,<sup>18</sup> have been used. The error involved in using the room-temperature values to interpret the low-temperature results is not considered to be serious. Using these parameters, best fits are obtained to the experimental results by means of a computer using the lines corresponding to values of  $m$  greater than  $m'$ . Several different values of  $m'$  are tried, and for  $r$  greater than  $20\text{--}25 \text{ \AA}$  only small changes in the constants resulted. These constants are the Van der Waals constant  $a$  and the quantity  $E_{\text{gap}} - (E_A + E_D)$ . Figure 8 shows the results of fitting the type  $I_A$  and  $II_A$  data. It is seen that a good fit is obtained for large  $r$ . The fit does not establish that the Van der Waals correction is the best one to use, and the plots show that for an approximate fit over the whole range the simple Coulombic term alone is adequate. The experimental results indicate that for  $r$  less than about  $10 \text{ \AA}$ , electrons and holes are not bound to the pairs. Thus the closely spaced pairs do not contribute to fluorescence. This may be partly because there are few of them in a random distribution, but it seems to be the case that for  $m$  numbers less than about six no binding will occur and so there will be no fluorescence. This may not be so for other materials with larger donor and acceptor binding energies.

As noted earlier, other crystals to which impurities have been added may give spectra which can be recognized as belonging to types I or II, but in which the corresponding lines have been shifted, and in which

the fine structure is different. The spectral types  $I_B$  and  $II_B$ , resulting from the addition of tellurium and cadmium are illustrated in Fig. 3. If the environment of corresponding lines in either class is examined they will be found to be very similar. If selenium is added a new spectrum results called  $I_C$ . The presence of lines of the  $I_A$  spectrum in the background of the other spectra shows that the addition of impurities does not displace those impurities already present, but merely overwhelms them. However, care has to be exercised in the doping process for too great concentrations rapidly lead to broadening of the lines and ultimately to the absence of fluorescence.

The shift of the lines within a given class of spectra reflects the fact that the donor or acceptor binding energies change from one impurity to another. Table I gives the parameters deduced by fitting all the results to Eq. (2). Because of the present uncertainty of the Van der Waals correction in Eq. (2), there may be an absolute error of about  $\pm 0.002 \text{ eV}$  in the values of  $E_{\text{gap}} - (E_A + E_D)$ . The band gap<sup>20</sup> of  $2.325 \pm 0.005 \text{ eV}$  is known much less accurately and consequently there may be a comparatively large absolute error in the values of  $(E_A + E_D)$ . The relative values are known with much greater precision. The chemical centers believed to be responsible for the spectra are also indicated in Table I; the reasons for these choices are given in Sec. F.

#### E. Annealing Results

Some annealing experiments were performed in an attempt to detect ion pairing effects as discussed by Reiss *et al.*<sup>21</sup> Sixteen h at  $400^\circ\text{C}$ , 16 h at  $700^\circ\text{C}$ , and 44 h at  $800^\circ\text{C}$  did not produce any marked changes in the pair spectra, for either type  $I_A$  or  $II_A$  crystals. Reiss *et al.*, said that two ions were "paired" if they fell within a distance  $b$  of each other and calculations were made of the fraction of the ions paired. This fraction depends on the temperature at which equilibrium is attained and the ion concentration. Since the latter quantity is not known in the present situation it is not possible to make precise calculations. However, we may tabulate a few numbers assuming that there are an equal number of donors and acceptors.

TABLE I. Parameters obtained by fitting results to Eq. (2).

| Dopant | Type   | $E_{\text{gap}} - (E_A + E_D)$<br>eV | $(E_A + E_D)$<br>eV | $a$ ( $\text{\AA}$ )<br>(Van der Waals<br>constant) | Acceptor<br>and<br>donor |
|--------|--------|--------------------------------------|---------------------|---|--------------------------|
|        |        | $\pm 0.002$                          | $\pm 0.007$         |   |                          |
| -      | $I_A$  | 2.1857                               | 0.1393              | 11.1  | Si + S                   |
| Te     | $I_B$  | 2.2007                               | 0.1243              | 8.62  | Si + Te                  |
| Se     | $I_C$  | 2.1873                               | 0.1377              |   | Si + Se                  |
| Zn     | $II_A$ | 2.1696                               | 0.1554              | 9.45  | Zn + S                   |
| Cd     | $II_B$ | 2.1368                               | 0.1882              | 6.58  | Cd + S                   |

<sup>20</sup> M. Gershenzon, D. G. Thomas, and R. E. Dietz, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 752.

<sup>21</sup> H. Reiss, C. S. Fuller, and F. J. Morin, *Bell System Tech. J.* **35**, 535 (1956).



TABLE II. Donor and acceptor concentration and pairing fraction.

| Temp. | $b$    | Concentration of donors and acceptors  | Fraction paired                                  |
|-------|--------|--|--|
| 800°C | 7.6 Å  | $\begin{cases} 10^{20} \text{ cm}^{-3} \\ 10^{18} \text{ cm}^{-3} \end{cases}$ | $\begin{cases} \sim 0.7 \\ \sim 0.1 \end{cases}$ |
| 500°C | 10.6 Å | $\begin{cases} 10^{19} \text{ cm}^{-3} \\ 10^{17} \text{ cm}^{-3} \end{cases}$ | $\begin{cases} \sim 0.7 \\ \sim 0.1 \end{cases}$ |
| 350°C | 13.1 Å | $\begin{cases} 10^{18} \text{ cm}^{-3} \\ 10^{16} \text{ cm}^{-3} \end{cases}$ | $\begin{cases} \sim 0.7 \\ \sim 0.1 \end{cases}$ |

The pair concentration is guessed to be below  $10^{17} \text{ cm}^{-3}$ ; thus at 500°C only about 10% will be paired. At temperatures lower than this the fraction paired will be larger, but the diffusion of substitutional impurities will be extremely slow. It should be noted that for the temperatures used, most, if not all, of the "paired" ions will be ineffective in producing recombination radiation since they are too close to bind holes or electrons. (If diffusion occurred at very low temperatures and all the ions became highly associated, the pair spectra would presumably disappear). These considerations show that it is not surprising that the annealing experiments described above did not produce marked changes in the spectra. In addition, since crystals when grown are customarily cooled relatively rapidly from 800°C, it is expected that the distribution of donors and acceptors will be random and so the intensity pattern of the lines should be the same from one crystal to another as observed.

#### F. The Identification of the Donors and Acceptors

Type  $I_A$  crystals are produced without the intentional addition of any impurities, and it is certainly of interest to know what donors and acceptors produce this spectrum. The following deductions may be made. The addition of zinc produces type  $II_A$  crystals, in which the donors and acceptors are on opposite lattice sites. Zinc is known to be an acceptor in GaP and must be on gallium sites. Consequently, the donor must be on phosphorus sites. The donor might be a phosphorus vacancy or an element such as sulfur from Group VI of the Periodic Table. Sulfur is a common impurity in the phosphorus from which the GaP is made, and for the moment we may assume that sulfur is the donor. It follows that for type  $I_A$  sulfur on phosphorus sites also constitutes the donor center. Since donors and acceptors for type  $I_A$  are on the same sites, the acceptor must be on a phosphorus site. Such an acceptor might be silicon, which could come from the  $\text{SiO}_2$  tubes in which the crystals are grown.

These tentative conclusions may be tested. Thus when sulfur and silicon were added as dopants it was found that type  $I_A$  crystals were still produced, although the lines were broadened and the over-all fluorescent

efficiency reduced at the higher concentrations. The fact that the addition of sulfur did not alter the spectral type, whereas the addition of selenium and tellurium resulted in new spectral types, is strong evidence that sulfur is indeed involved in the type  $I_A$  spectra. (It might be noted that capacitance measurements indicate that all three of these impurities are quite soluble in GaP.) Since spectra involving Group IV elements other than silicon have not yet been produced, the same argument in favor of silicon as the acceptor is not possible. However, as noted earlier, when  $\text{Al}_2\text{O}_3$ , BN, or AlN crucibles are used instead of  $\text{SiO}_2$  tubes to contain the gallium solutions, relatively weak fluorescence is generally seen, but if pieces of  $\text{SiO}_2$  are added to the solution during growth the  $I_A$  spectra are usually more intense. We may provisionally accept, therefore, that Si is the acceptor. It follows that  $I_B$  and  $I_C$  spectra arise from Si-Te and Si-Se pairs, respectively, and  $II_B$  from Cd-S pairs, as indicated in Table I.

If accurate Hall data were available, it would be interesting to compare the sum of the acceptor and donor binding energies as determined from Hall measurements and from the optical data. At present, all one can say is that the approximate Hall data seem to be consistent with the optical results. Thus, the Hall measurements yield binding energies of sulfur, zinc, and cadmium of about 0.10, 0.04, and 0.08 eV, respectively.<sup>22</sup> These results lead to predicted ( $E_A + E_D$ ) values for types  $II_A$  and  $II_B$  spectra of 0.14 and 0.18 eV, which compare favorably with the observed values of 0.155 and 0.188 eV, respectively.

#### G. Broad Emission

The discussion so far has considered only the sharp pair lines, but as Figs. 2 and 3 show, there is in addition much broad background radiation, and, as mentioned above, if the exciting intensity is reduced the sharp lines disappear into the broad emission. Figures 2 and 3 show that for the approximately constant exciting intensity used to obtain these results, the peak of the broad emission changes as the crystal doping changes. Furthermore, the shift of the broad peak corresponds closely to the change in the quantity ( $E_A + E_D$ ). Table III illustrates this, and also gives values of  $r$  for an isolated pair which would radiate at an energy equal to that of the position of the broad peak. Though the position of

TABLE III. Peak shift and isolated pair  $r$  value.

| Type   | $[E_{\text{gap}} - (E_A + E_D)]$<br>eV | Position of Broad Peak<br>eV | Position of peak minus<br>$[E_{\text{gap}} - (E_A + E_D)]$<br>eV | $r$<br>calc. for pair at peak<br>Å |
|--------|--|------------------------------|--|------------------------------------|
| $I_A$  | 2.1857                                 | 2.213                        | 0.027  | 53                                 |
| $I_B$  | 2.2007                                 | 2.226                        | 0.025  | 57                                 |
| $I_C$  | 2.1873                                 | 2.213                        | 0.026  | 55                                 |
| $II_A$ | 2.1696                                 | 2.200                        | 0.030  | 48                                 |
| $II_B$ | 2.1368                                 | 2.167                        | 0.030  | 48                                 |

<sup>22</sup> M. Gershenzon and H. C. Montgomery (unpublished).

the peak shifts with doping, the value of  $r$  remains nearly constant at about 50 Å. This observation strongly suggests that the broad emission and the pair lines are intimately connected.

If the concentration of pairs is taken to be  $10^{17}/\text{cc}$ , the average separation between atoms is in the vicinity of 200 Å. It might be asked why the radiation intensity is not most intense at a wavelength corresponding to this separation; for the first holes and electrons created by the excitation would occupy these pairs which are numerically the most probable pairs. Such pairs, however, would not be *isolated* pairs (i.e., pairs with a separation very small compared to the distance between the pair and any other donor or acceptor) and consequently, sharp lines would not result. For pairs with large (typical) separations, however, the overlap between the wave functions of the trapped holes and electrons will be very small and as a result the radiative lifetimes will be long. Consequently, the distant pairs may become saturated, and the extra holes and electrons will be forced to find the less likely, more closely spaced pairs. The oscillator strength associated with such pairs will, as  $r$  decreases, increase more rapidly than the numbers of pairs decrease, since the overlap will vary exponentially with  $r$  for separations greater than the sum of the donor and acceptor radii (which are of the order of 20 Å). Thus, considerable energy can be radiated by the isolated pairs.

This situation can at least qualitatively explain the relevant observations. As the exciting intensity is reduced, the more probable nonisolated pairs will be able to radiate sufficient energy so that the closer pairs are not significantly excited—still, however, the very distant pairs will be saturated. On further lowering the intensity, the peak of the emission will move to longer wavelengths as fewer and fewer of the distant pairs are saturated. This, presumably, is the explanation of the data shown in Fig. 5, in which the peak shifts from a position calculated to correspond to 48 Å, to one calculated to be 120 Å. Presumably at infinitely low level excitation, radiation would occur at an energy determined by the mean separation. In these considerations it has been assumed that once a carrier has been trapped it can do nothing but radiate. At low temperatures, when  $kT$  is very much less than the donor and acceptor binding energies, and at low concentrations when tunneling may not be important, these assumptions seem reasonable. At higher temperatures carriers will spend less time trapped, and will be able to migrate to nonradiative recombination centers, and therefore the radiative efficiency diminishes.

#### H. Flash Excitation

If the crystals are excited by a powerful flash of light lasting a few microseconds, and a photograph is taken of the total emitted radiation, as shown in Fig. 6, the broad emission is seen. No pair lines are apparent and

the bound exciton radiation is much enhanced. Presumably during the flash all donors and acceptors are neutralized and there is negligible decay. Excess holes and electrons form excitons bound to impurities which decay comparatively very rapidly, because the electrons and holes have a much larger degree of overlap than they would have when associated with pairs. The spectrum of the emitted light is thus expected to show strong bound exciton contributions and contributions from the pairs which reflect quite simply the probability distribution of the pairs, for on this model each pair will decay just once. The observed absence of the rare pair lines, and the shift of the broad peak to long wavelengths is in qualitative agreement with these expectations.

The decay of the broad fluorescence after the termination of the flash excitation has been studied. No marked differences are seen between 20 and 4.2°K, and for the pure type  $I_A$  crystals at least, the eye can detect green light emission for many seconds after the flash. As might be expected, the decay kinetics are not simple. The decay has been followed at various wavelengths within the broad band and marked differences are observed; at no point is there a simple exponential time decay; rather, power laws are obeyed. It might be thought that at a particular wavelength a simple decay should occur, but that this need not be so for nonisolated pairs can be seen as follows. Imagine a colinear grouping of one acceptor and two donors, with separations large compared to the donor and acceptor radii. At some stage in the decay these may share one hole and one electron. Considering only electrostatic forces, the energy of the system will be independent of which donor the electron occupies. However, the overlap between the electron and the hole on the acceptor will depend very much on which donor is occupied, so that there can be two lifetimes at the same energy. If the situation is now imagined in three dimensions, it is clear that there can be many lifetimes at a particular energy. Since in the initial condition all donors and acceptors are neutral, the situation just described will only occur at some subsequent stage in the decay. This variation of the conditions during the decay will certainly also complicate the analysis, and in addition the decay will vary from one crystal to another since it will depend on the concentration of the impurities present. No deep understanding of the decay kinetics can be claimed at present, but the observations do not seem to be explicable in terms of a simple optical transition, and the model proposed might very well explain them. The scheme of nonisolated pairs giving rise to many overlapping energy levels provides a natural explanation for the essentially temperature-independent width of the broad emission.

It is tempting to suggest that analogous "edge" emission in other semiconductors may have a similar origin. Thus, the time decay of the emission of CdS has been observed and found not to be a simple exponential but is more nearly a power law decay. The position of

the emission and the large binding energy of acceptors in CdS would indicate that the ground state of the acceptors is not involved, but rather an excited state, the decay of the hole to the acceptor ground state being impeded by the large amount of energy which has to be lost presumably by phonon emission.

The absence of any reports of absorption corresponding to the broad emission, at least in the lightly doped crystals is understandable in terms of the very weak oscillator strength indicated by the long lifetimes. The usefulness of the fluorescence lies in the fact that weak lines can be seen, since once the centers have been excited they ultimately will radiate.

### SUMMARY

Crystals of GaP grown from gallium solution frequently show strong fluorescence at low temperatures. This fluorescence contains many sharp lines which have been proved to arise from the recombination of an electron on a donor recombining with a hole on an acceptor. Sharp lines result because the energy depends on the separation, and since the donors and acceptors fall on lattice sites, the separations can only have discrete values. From the intensity pattern of the lines, assuming a random distribution of impurities, the geometrical arrangement of the impurities may be deduced and any line may be identified with a particular separation. The addition of added impurities during growth produce different spectra because different donors and acceptors become involved. There is fine structure in the spectra. From the spectra considerable information may be deduced concerning the chemical nature of the impurities. Thus the emission from "pure" material probably arises from Si-S pairs. In addition to the lines there is broad emission and as the line spectra change with doping so does this broad emission. Consequently, it is concluded that the latter arises from recombination at nonisolated widely separated pairs. It is found that the position of the broad band in a particular crystal changes as the exciting intensity changes, and the time decay of these bands after flash excitation is very complex. These observations appear to be compatible with recombination at nonisolated pairs.

### ACKNOWLEDGMENTS

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### APPENDIX: ILLUSTRATION OF THE CALCULATION OF $N(r)$ FOR THE TYPE I GEOMETRY

The type I geometry has both donors and acceptors on the same type of sites of the GaP lattice (zincblende structure). This leads to an fcc lattice. In this lattice, if one atom is at (0,0,0), another will have the coordinates  $(n_1, n_2, n_3)$ , where the  $n$ 's are integers, and satisfy the relations,

$$n_1 + n_2 + n_3 \text{ is even;} \quad (\text{A1})$$

$$n_1^2 + n_2^2 + n_3^2 = 2m, \quad (\text{A2})$$

where  $m$ , the "shell number," is an integer. The separation  $r$  between the pairs is given by

$$r = (\frac{1}{2}m)^{\frac{1}{2}}a_0,$$

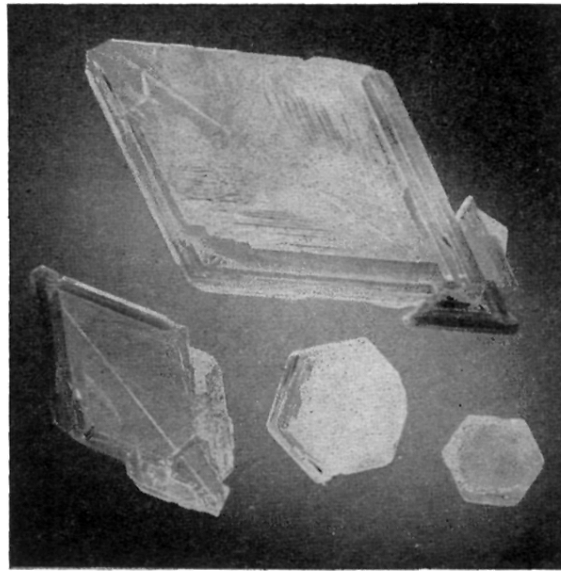
where  $a_0$  is the GaP lattice constant. It is necessary to determine what integers satisfy (A1) and (A2) for each value of  $n$ , and for a particular set of such numbers, there will be  $N(r)'$  arrangements. The sum of the  $N(r)'$  for a particular  $r$  becomes  $N(r)$ . A few results are shown in Table IV. It happens that when  $2m = 4^l(8k+7)$

TABLE IV. Tabulated  $N(r)$  values.

| $m$ | $n_1$   | $n_2$ | $n_3$  | $N(r)'$    | $N(r)$ |
|-----|---------|-------|--------|------------|--------|
| 13  | {5<br>4 | 1     | 0      | {24<br>48} | 72     |
| 14  | ...     | ...   | ...    | ...        | 0      |
| 15  | 5       | 1     | 2      | 48         | 48     |
| 16  | 4       | 4     | 0      | 12         | 12     |
| 17  | {5<br>4 | 3     | 0<br>3 | {24<br>24} | 48     |

where  $l$  and  $k$  can have values 0, 1, 2, ...,  $N(r)$  equals zero.

The type II arrangement is slightly more complicated but proceeds similarly; now all values of  $m$  have non-zero  $N(r)$  values.



1 CM

FIG. 1. Some typical crystals of GaP grown from Ga solution using the slow-cooling technique.