

if  $T_d'$  is lower than  $\bar{T}_d$  by about 1 eV or more, this would be detected from the shape of the curves for the two faces. Within this limit then, the displacement energy for indium is a minimum in the  $\langle 111 \rangle$  direction in InSb.

## VI. CONCLUSIONS

(1) The defects which annihilate in stage I in InSb are produced by the displacement of antimony atoms and those which annihilate in stage II are produced by the displacement of indium atoms.

(2) The threshold displacement energy for indium in InSb is about 6.4 eV and the threshold displacement energy for antimony lies between about 8.5 eV and 9.9 eV.

(3) The likely direction of minimum displacement energy in InSb is the  $\langle 111 \rangle$  direction.

## ACKNOWLEDGMENT

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## Direct Transition and Exciton Effects in the Photoconductivity of Gallium Phosphide

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Photoconductivity spectra between 0.6 and 3.3 eV of vapor-grown, high- and low-resistivity, GaP whiskers and of high-resistivity floating-zone-refined crystals of GaP were measured as a function of temperature. Structure seen in the spectra of high-resistivity whiskers and interpreted as direct exciton formation (with subsequent dissociation) permitted a determination of the energy gap at  $\mathbf{k}=0$  and its temperature variation. It could be fitted by  $E_G=2.895\pm 0.004 - (1.17\pm 0.01)\times 10^{-6} T^2$  in eV for temperature below 300°K. This structure was seen as a result of an anomalously large photoconductive response in the direct transition region, which was attributed to a mobility increase from optical excitation similar to that seen previously in InP, CdSe, and GaAs. In low-resistivity, sulfur-doped whiskers photoconductivity arising from absorption in bound exciton states associated with neutral sulfur donors was observed. The photoconductive lifetime at 296°K in high-resistivity whiskers was found to be  $3\times 10^{-9}$  sec.

## INTRODUCTION

THE fundamental absorption edge of gallium phosphide arises from indirect transitions from the valence-band maximum to conduction-band minima in the  $[100]$  directions.<sup>1,2</sup> The forbidden energy gap between these band extremes is  $2.325\pm 0.003$  eV at 0°K.<sup>3</sup> The determination of the energy gap at  $\mathbf{k}=0$  ("the direct band gap") has been a more difficult task. A number of experiments<sup>2,4-6</sup> aimed at its determination have not definitely located it. Observation of direct transitions in optical absorption<sup>2</sup> has been prevented by difficulties in preparing GaP crystals less than  $8\mu$  in thickness with polished faces. This limited the study of absorption to absorption coefficients below  $8\times 10^3$  cm<sup>-1</sup>. On the other hand, absorption coefficients somewhat greater than this are necessary to be observable

in reflectivity measurements. Recently, however, a very weak maximum in the reflectivity has been observed<sup>7</sup> at 2.8 eV at 300°K. From its pressure dependence it was identified as due to the direct band gap.

The first report in the literature concerning the direct band gap in GaP was that of Spitzer *et al.*<sup>2</sup> They observed an absorption band in the infrared near  $3\mu$  which was present only in *n*-type material. This indicated a conduction-band minimum about 0.31 eV above the  $[100]$  minima. They also observed enhanced absorption at 0.35 eV above the forbidden gap energy in a study of the fundamental absorption edge. They suggested that the observed conduction-band minimum at 0.31 to 0.35 eV above the  $[100]$  minima was that at  $\mathbf{k}=0$ .

The lack of a significant wavelength shift of the  $3\text{-}\mu$  absorption band with pressure led Paul and Zallen<sup>6</sup> to conclude that the higher conduction band minima responsible lay directly above the  $[100]$  minima rather than at  $\mathbf{k}=0$  (see Fig. 1).

Allen and Hodby<sup>8</sup> studied the shift of the  $3\text{-}\mu$  band

<sup>1</sup> A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, *Phys. Chem. Solids* **11**, 140 (1959).

<sup>2</sup> W. G. Spitzer, M. Gershenzon, C. J. Frosch, and D. F. Gibbs, *Phys. Chem. Solids* **11**, 339 (1959).

<sup>3</sup> M. Gershenzon, D. G. Thomas, and R. E. Dietz, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 752.

<sup>4</sup> H. G. Grimmeiss, W. Kischio, and H. Koelmans, *Solid State Electron.* **5**, 155 (1962).

<sup>5</sup> W. Paul, *J. Appl. Phys.* **32**, 2082 (1961).

<sup>6</sup> W. G. Spitzer and C. A. Mead, *Phys. Rev.* **133**, A872 (1964).

<sup>7</sup> R. Zallen and W. Paul, *Phys. Rev.* **134**, A1628 (1964). *Note added in proof.* Gross and co-workers {E. F. Gross, N. S. Kochneva, and D. S. Nedzvetski, *Dokl. Akad. Nauk SSSR* **153**, 574 (1963) [English transl.: *Sov. Phys.—Dokl.* **8**, 1103 (1964)]} recently reported a peak in the reflectivity spectrum of GaP at 2.858 eV at 77°K.

<sup>8</sup> J. W. Allen and J. W. Hodby, *Phys. Soc. (London)* **82**, 315 (1963).

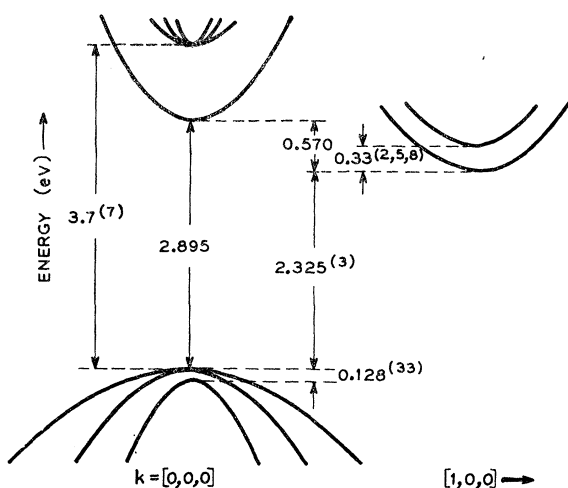


Fig. 1. Energy-band structure in  $k$  space for GaP as presently known. Energy gaps are given for  $0^\circ\text{K}$  for those where the temperature dependence has been measured.

as a function of composition of GaAs-GaP alloys and concluded that the Paul model was correct except that the initial states of the absorptive transition were shallow donors connected with the  $[100]$  band minima rather than the band minima themselves. This conclusion was consistent with the observation of Spitzer *et al.*<sup>2</sup> that the strength of the  $3\text{-}\mu$  band did not diminish from carrier freeze-out as the temperature was lowered. Thus, it can be concluded that the band minimum originally observed by Spitzer *et al.*<sup>2</sup> is not the one at  $\mathbf{k}=0$ .

A study of the photovoltaic effect by Grimmeiss<sup>9</sup> and co-workers originally found only a single peak (at 2.95 eV) in the intrinsic absorption region. Photovoltaic spectra taken later<sup>4,10</sup> showed a shoulder at 2.4 eV due to indirect transitions, a peak attributed to direct transitions at 2.8 eV, and a shoulder at 2.95 eV.

Recently, Spitzer and Mead<sup>6</sup> have studied the photovoltaic effect with surface barrier junctions on GaP. They found the onset of direct transitions to occur at  $0.45 \pm 0.04$  eV above the onset of indirect transitions. By assuming no contribution from direct exciton formation, they interpret this as the energy separation between the band minima at  $[000]$  and those in the  $[100]$  directions. In view of the present work, this assumption is open to question.

A very recent measurement of the reflectivity spectrum of GaP by Zallen and Paul<sup>7</sup> has shown a very weak maximum at 2.8 eV. They interpret this as due to the direct transition edge because of the size and sign of its pressure shift.

In the work reported here, a peak in the photoconductive response was found at the edge of the direct-transition region. This was interpreted as the formation

of direct excitons, the ionization of which produced a photocurrent. The shift in energy of this peak with changing temperature was found to be the same within experimental error as that for the indirect band gap.<sup>8</sup> By estimating the binding energy of the direct exciton to be 0.013 eV, the direct band gap was deduced to be  $2.895 \pm 0.004$  eV at  $0^\circ\text{K}$ . The band minimum at  $\mathbf{k}=0$  is thus 0.570 eV higher than those in the  $[100]$  directions.

In addition to these results, measurements of the photoconductivity lifetime at  $296^\circ\text{K}$  in GaP are reported; identification of a photoconductivity response peak as resulting from absorption in a neutral, immobile complex (an exciton bound to a neutral sulfur atom) is presented; and an explanation is proposed for the anomalously large photoconductive response in the direct-transition region in high-resistivity GaP whiskers.

#### EXPERIMENTAL TECHNIQUE

The GaP crystals used in this study were of three types: high-resistivity ( $\sim 10^7 \Omega\text{-cm}$  at  $296^\circ\text{K}$ ), undoped, vapor-grown whiskers<sup>11</sup>; low-resistivity ( $\sim 0.2 \Omega\text{-cm}$  at  $296^\circ\text{K}$ ), sulfur-doped, vapor-grown whiskers<sup>11</sup>; and high-resistivity ( $\sim 10^8 \Omega\text{-cm}$  at  $296^\circ\text{K}$ ), undoped, floating-zone-refined, single crystals. Both high- and low-resistivity whiskers were  $n$  type, about 0.1 cm in length ( $\langle 111 \rangle$  crystallographic direction), and triangular in cross section with sides ( $\{201\}$  or  $\{2\bar{1}\bar{1}\}$  faces) of about 0.005 cm. The zone-refined crystals were  $p$  type, about 0.1 cm long and 0.02 cm in lateral dimensions and had etched surfaces.

Contacts were made to  $n$  type whiskers by alloying silver paste with added tellurium at  $800^\circ\text{C}$  in a forming gas ( $\text{N}_2:\text{H}_2::9:1$ ) atmosphere. For  $p$ -type crystals, zinc was added to the silver paste. These contacts produced a linear voltage-current characteristic for voltages up to 1000 V, a typical voltage applied to the crystals while measuring photoconductive spectra. No photovoltaic effect was observed when the entire crystal plus contacts were illuminated. A scan of a point of light along a whisker showed the photoconductive response to be uniform along the crystal and to fall smoothly to zero as the spot passed the contacts.

For measuring the photoconductive spectra light from a ribbon-filament tungsten lamp was passed through a Perkin-Elmer Model 112 quartz prism monochromator and focused onto the GaP crystal mounted in a cold finger-type Dewar. Care was taken to illuminate the crystals uniformly to avoid space-charge effects.

The voltage built up across a  $5\text{-M}\Omega$  resistor in series with the GaP crystal was fed into the lead sulfide cell input of the Perkin-Elmer electronics. This voltage was directly measured for lifetime measurements, and the

<sup>9</sup> H. G. Grimmeiss and H. Koelmans, Philips Res. Rept. **15**, 290 (1960).

<sup>10</sup> H. G. Grimmeiss, A. Rabenau, and H. Koelmans, J. Appl. Phys. **32**, 2123 (1961).

<sup>11</sup> M. Gershenzon and R. M. Mikulyak, J. Electrochem. Soc. **108**, 548 (1961).

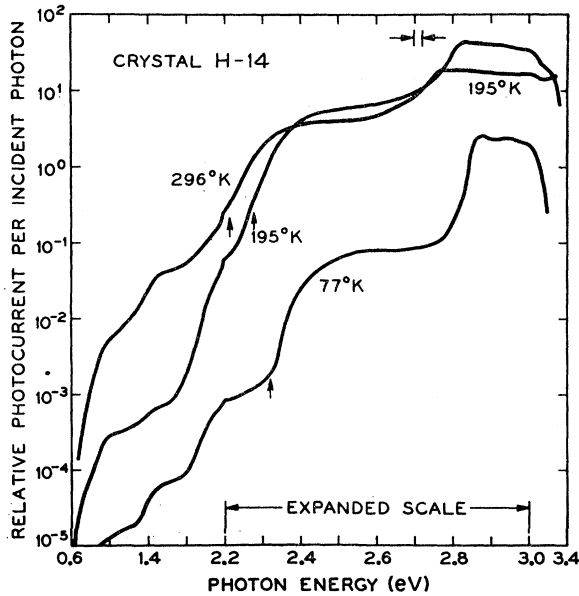


FIG. 2. Photoconductive spectra for an *n*-type, high-resistivity ( $8.3 \times 10^6 \Omega\text{-cm}$  at  $296^\circ\text{K}$ ) GaP whisker. The cusps in the curves at 2.2 and 3.0 eV arise from the scale expansion between these photon energies. The arrows near 2.3 eV indicate the energy of the forbidden gap at the various temperatures. Over 100 experimental points have been used in drawing each curve. (The latter remarks apply also to Figs. 3, 4, 6, and 7.)

light intensity striking the crystal was determined with a thermocouple, calibrated against a standard black body, and placed in the position of the crystal.

#### DIRECT BAND GAP

Figure 2 is a plot of the relative photocurrent per incident photon versus photon energy for a high-resistivity GaP whisker. There are three regions in the response curve: the extrinsic or impurity absorption region and the intrinsic absorption regions due to indirect and direct valence-band-conduction-band transitions. The extrinsic region extends below about 2.2 eV and contains a number of edges due to absorption involving different defect centers. The photoconductive response in this region is very low since most of the incident photons pass through the crystal without being absorbed. The indirect-transition region begins at 2.2 or 2.3 eV (depending on temperature) and extends to about 2.7 or 2.8 eV. The increasing response in this region is due to the increasing absorption coefficient and follows roughly the ratio of absorbed light to incident light, assumed to strike the front crystal face perpendicularly,

$$\frac{I_A(\nu)}{I_0(\nu)} = \frac{[1-R(\nu)][1-e^{-\alpha(\nu)L}]}{1-R(\nu)e^{-\alpha(\nu)L}}, \quad (1)$$

where  $R$  is the reflectivity,  $\alpha$  the absorption coefficient of GaP,  $\nu$  the light frequency, and  $L$  the perpendicular

distance from a whisker face to its back edge. At the high-energy edge of the indirect-transition region, all of the light entering the crystal is absorbed. In spite of this fact, the photoconductive response increases a further factor of between 10 and 100 (depending on temperature) in the direct-transition region, which extends above 2.7 or 2.8 eV.

The origin of this anomalous response is the subject of the following section. For the purpose of the present section it is only necessary to realize that the two properties of the light which could initiate the anomalous response are its frequency or possibly its intensity. The intensity of the light (originating from a tungsten filament) decreases monotonically with increasing frequency throughout the indirect- and direct-transition regions. It does not seem possible that a slowly and smoothly decreasing intensity could cause a sharp rise in response which would possess structure near its peak. [The intensity is, of course, divided into the measured photocurrent to obtain the ordinate of Fig. 2.] On the other hand, the changing frequency of the light can effect the photocurrent through the absorption coefficient which is expected to increase rapidly with frequency in the direct-transition region. The decreasing absorption depth causes an increasing excitation density which can lead to a number of alterations in the conduction process (e.g., mobility changes) that will enhance the photoconductive response. What is to be emphasized here is simply that a change in response in the direct-transition region still reflects a change in the absorption coefficient.

With this point of view in mind, note in Fig. 2 the very sharp rise of the response near 2.7 eV (at  $77^\circ\text{K}$ ) to a peak at 2.875 eV followed by a relatively flat portion and then a decrease at the highest energies studied. The sharp rise, the peak, and the mild dip following are similar to the behavior of the absorption coefficient for direct transitions in GaAs,<sup>12</sup> Ge,<sup>13</sup> and GaSb.<sup>14</sup> The absorption peak found in these materials is due to the formation of direct excitons. The steepness of the absorption edge depends on the amount of broadening of the direct exciton-absorption line. In the case<sup>12</sup> of GaAs the steepness of this rise increases and the peak becomes more prominent as the temperature is lowered. These effects are also very prominent in Fig. 2. While the absorption coefficient in GaAs increases slowly according to  $(h\nu - E_G)^{1/2}$  following the dip on the high-frequency side of the direct-exciton peak,<sup>12</sup> such a rise was not observed in the present experiment. This is believed due to surface recombination which is expected to become important at the highest photon energies where

<sup>12</sup> M. D. Sturge, Phys. Rev. **127**, 768 (1962).

<sup>13</sup> G. G. MacFarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Proc. Roy. Soc. (London) **71**, 863 (1958).

<sup>14</sup> E. J. Johnson, I. Filinski, and H. Y. Fan, *Proceedings of the International Conference on the Physics of Semiconductors*, Exeter (The Institute of Physics and the Physical Society, London, 1962), p. 375.

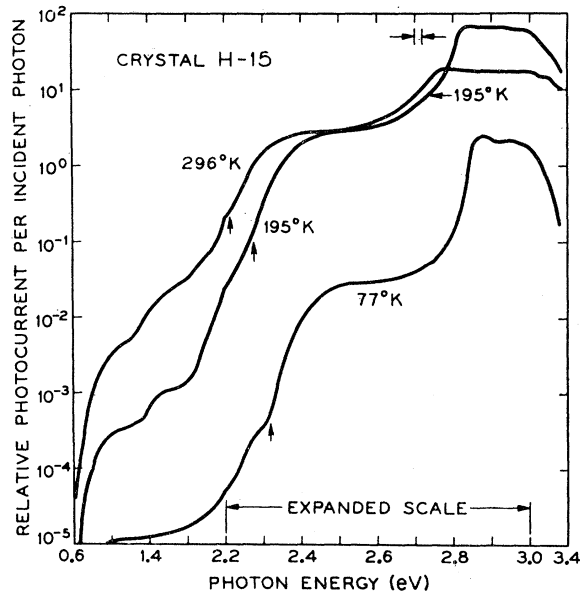


FIG. 3. Photoconductive spectra for an *n*-type high-resistivity ( $10^7 \Omega\text{-cm}$  at  $296^\circ\text{K}$ ) GaP whisker.

absorption coefficients are largest. Surface recombination should cause a greater decrease in the response at lower temperatures since a lower diffusion constant diminishes carrier migration away from the surface where carrier lifetimes are shorter than in the crystal interior. This effect is observed in Fig. 2 and supports the interpretation that the response falloff is due to surface recombination.

The structure in the photoconductivity response curves was reproducible for a given high-resistivity whisker and between different high-resistivity whiskers. Figures 3 and 4 are photoconductive spectra for two different crystals. The amount of surface recombination is the main variant between crystals, being more prominent for the whisker of Fig. 4. Several other whiskers have shown response curves nearly identical to those of Figs. 2, 3, and 4. Also, no shift in frequency of the peak of the anomalous response was observed for changes in the light intensity from the tungsten lamp by factors of two. For one whisker the photoconductive spectrum was measured using the much more intense light from a mercury arc. A comparison of this spectrum with that using the tungsten lamp showed the photoconductive response to be rising linearly with the light intensity in the normal response region, consistent with Eq. (1), but rising somewhat superlinearly (photocurrent proportional to the 1.3 power of the light intensity) near the peak of the anomalous response region. No significant shift in frequency of the peak was seen.

We therefore interpret the peak in the photoconductive response of high-resistivity whiskers of GaP to be due to the formation of direct excitons followed by their dissociation into current carriers. The dissociation occurs either by emission or absorption of phonons

of appropriate wave vector or by interaction with an impurity center.<sup>15</sup> The dissociation processes give rise to the broadening (lifetime broadening) of the exciton absorption line and their temperature dependence causes the decreasing slope of the direct-transition edge with increasing temperature in the photoconductive spectra.<sup>15</sup>

The direct energy gap is the sum of the direct-exciton formation energy found from the peaks in Figs. 2, 3, and 4 plus the direct-exciton binding energy which is estimated to be 0.013 eV in the Appendix. Values of the direct energy gap deduced in this manner for each temperature studied are plotted in Fig. 5. The solid line fitted to the points is given by

$$E_G(T) = 2.895 \pm 0.004 - (1.17 \pm 0.01) \times 10^{-6} T^2 (\text{eV}) \quad (2)$$

for  $T \leq 300^\circ\text{K}$ . The errors have been determined from the errors in the experimental points and from the estimated uncertainty in the direct exciton binding energy. The temperature-dependent term is the same as that found to hold (at least for  $T \lesssim 100^\circ\text{K}$ ) for the indirect gap.<sup>3</sup> Zallen and Paul<sup>7</sup> found that the direct gap shifted with a slope of  $-4.6 \times 10^{-4} \text{ eV}/^\circ\text{K}$  near room temperature. A dashed line of this slope is shown in Fig. 5. It can be seen from this figure that the temperature dependence of the direct gap found here is in agreement with that found by Zallen and Paul.<sup>7</sup>

The energy difference between the direct and indirect gaps<sup>3</sup> was found from this work to be 0.570 eV. This

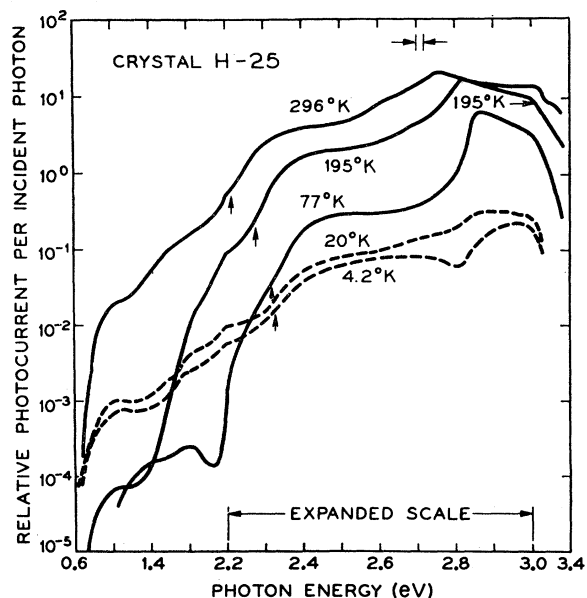


FIG. 4. Photoconductive spectra for an *n*-type high-resistivity ( $10^7 \Omega\text{-cm}$  at  $296^\circ\text{K}$ ) GaP whisker. Since the signal-to-noise ratio was only about 2 to 1 for much of the  $20^\circ\text{K}$  and  $4.2^\circ\text{K}$  data, the detailed shape of these spectra is considerably less trustworthy than those at higher temperatures.

<sup>15</sup> T. P. McLean and E. G. S. Paige, *Phys. Chem. Solids* **23**, 822 (1962).

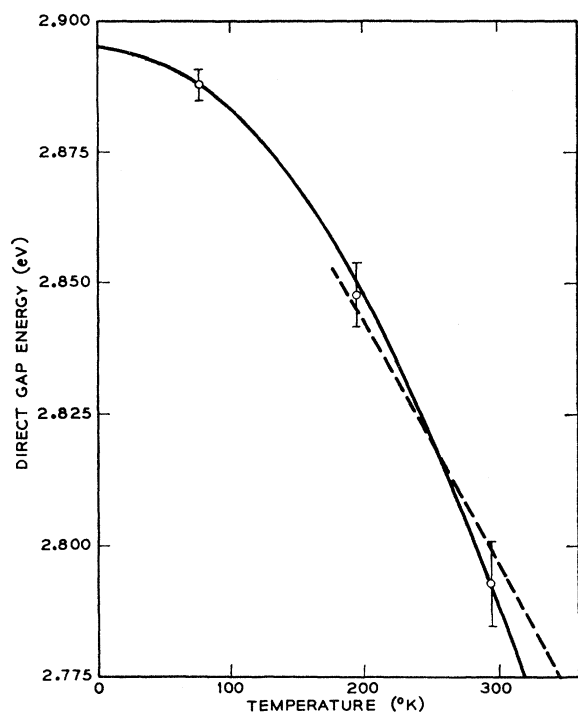


FIG. 5. Plot of experimental values of the forbidden energy gap at  $k=0$  versus temperature. The solid curve is  $E_g(T) = 2.895 - 1.17 \times 10^{-6} T^2$ . The dashed line has a slope of  $-4.6 \times 10^{-4} \text{ eV}/^\circ\text{K}$  and represents the variation of the energy gap at  $k=0$  with temperature as found by Zallen and Paul (Ref. 7).

value is in fine agreement with that of Zallen and Paul<sup>7</sup> found from reflectivity, but considerably higher than other previously reported values.<sup>4,6</sup> The data of Spitzer and Mead, however, are believed consistent with this value since it was their assumption of no direct-exciton contribution to the photovoltaic effect at the direct-transition edge which led to their lower value. Also, it seems that the data of Grimmeiss and co-workers<sup>4,9,10</sup> are not inconsistent with our value because of the difficulty in interpreting the shape of their photovoltaic response curves.

On the basis of the above findings, increased absorption in the infrared at energies above 0.570 eV would be expected in  $n$ -type material corresponding to transitions from the [100] minima to the [000] minimum. Since such transitions would require phonon participation, they would be considerably weaker than the transitions between the split [100] minima which they would partially overlap. Observation of such a band is thus expected to be difficult. Actually, an absorption band has been observed<sup>16</sup> near the appropriate energy in  $n$ -type GaP. It was not found, however, to be present in all  $n$ -type material and its presence was, in fact, correlated<sup>16</sup> with the occurrence of luminescence from a deep donor some 0.4 eV below the [100] minima.

<sup>16</sup> M. Gershenzon and R. M. Mikulyak, *Solid State Electron.* 5, 313 (1962).

It is interesting to note that there is an inflection point in the response curves of Figs. 2-4 at an average energy of 0.29 eV above the indirect gap energy which indicates the onset of additional absorption. Spitzer *et al.*<sup>2</sup> found this energy to be about 0.35 eV. Whether this increased absorption is due to transitions from the valence band to the higher lying [100] minima or to a very broad tail of the direct exciton cannot be determined from the photoconductive spectra. The recent measurements of the effect of pressure on the absorption by Zallen and Paul<sup>7</sup> point strongly to the latter process.

### ANOMALOUS RESPONSE

The response in the direct-transition region was termed anomalous in the last section because it increased 10 to 100 times over that in the indirect-transition region, even though all the light entering the crystal was absorbed in both regions. This response is also anomalous because it has been observed only in undoped, high-resistivity whiskers. Note the absence of the anomalous response in the photoconductive spectrum of an undoped, high-resistivity crystal cut from a floating-zone-refined ingot shown in Fig. 6. Since the model to be proposed for the anomalous response suggests it would occur in high-resistivity crystals such as this, its absence here can be attributed only to strong surface recombination. Such is expected<sup>17</sup> for etched surfaces as compared to the naturally grown crystal faces of the high-resistivity whiskers. No anomalous response was found in the photoconductivity spectrum

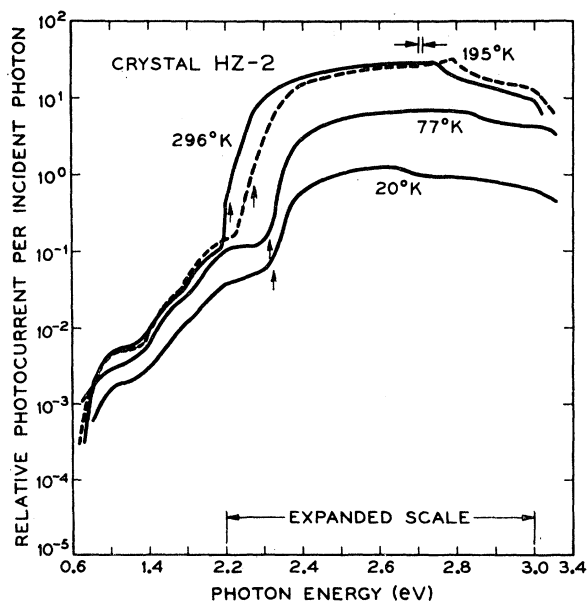


FIG. 6. Photoconductive spectra of a  $p$ -type, high-resistivity ( $10^8 \Omega\text{-cm}$  at  $296^\circ\text{K}$ ), zone-refined crystal of GaP.

<sup>17</sup> E. F. Gross and B. V. Novikov, *Phys. Chem. Solids* 22, 87 (1961).

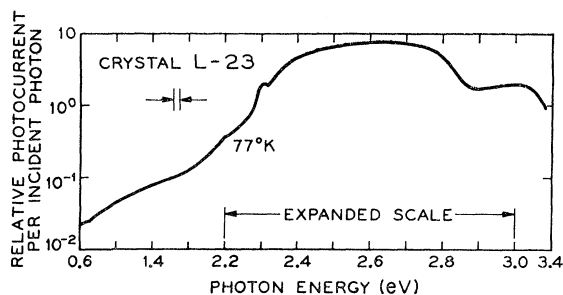


Fig. 7. Photoconductive spectrum of an *n*-type, low-resistivity ( $0.1 \Omega\text{-cm}$  at  $296^\circ\text{K}$ ), sulfur-doped GaP whisker at  $77^\circ\text{K}$ .

of a sulfur-doped, low-resistivity whisker shown in Fig. 7. It is interesting to note that the response for this crystal passes through a minimum very near  $2.875 \text{ eV}$ , the direct-exciton formation energy. This is attributed to the combined effects of surface recombination and the passage of the absorption coefficient through a maximum at that point. The anomalous response was also not observed in the photoconductivity spectrum of a low-resistivity GaP crystal reported by Nasledov and Slobodchikov.<sup>18</sup>

It was concluded in the previous section that this anomalous response resulted from the large absorption coefficient associated with direct transitions even through all of the light was already being absorbed for smaller values of the absorption coefficient. This being so, the photoconductive response can change only if the lifetime or the mobility of the carriers changes. These could depend on the absorption process in one of three ways: through conduction occurring in the  $[000]$  minimum, through spatial effects due to absorption near the surface, or through high-excitation density effects resulting from the minute absorption depth.

The mobility in the  $[000]$  minimum could be expected to have a value ten times larger than the  $[100]$  minima, or about  $10^3 \text{ cm}^2/\text{V-sec}$  at  $296^\circ\text{K}$ . For the response to increase by a factor of ten as at  $296^\circ\text{K}$  for crystal H-15 shown in Fig. 2 would require the lifetime in the  $[000]$  and  $[100]$  minima to be comparable. In the next section it is shown that the latter is about  $3 \times 10^{-9} \text{ sec}$ , a value which is at least  $10^3$  times longer than the relaxation time from the  $[000]$  minimum to the  $[100]$  minima.<sup>15</sup> Also, if the anomalous response results from a larger value of the mobility-lifetime product in the  $[000]$  minimum, it would seem difficult to account for the direct-exciton structure. Thus, we rule out this model as an explanation.

The anomalous response might be attributed to a lifetime lengthening caused by the saturation of a surface distribution of recombination centers. However, for this to occur at the light intensity  $I$  and lifetime  $\tau$  present in these experiments (see the following section),

<sup>18</sup> D. N. Nasledov and S. V. Slobodchikov, *Fiz. Tverd. Tela* **4**, 3161 (1962) [English transl.: *Soviet Phys.—Solid State* **4**, 2315 (1963)].

the number of surface recombination centers would be of the order of  $I\tau/h\nu \approx 10^4 \text{ cm}^{-2}$ . This is at least  $10^5$  times smaller than reasonable values. It is difficult to say if the surface space charge layer plays a significant role in the anomalous response, since its depth for such a high-resistivity crystal is determined by the density of trapped charge, an unknown quantity. Thus, it is not known whether the space-charge depth is comparable to the absorption depth in the anomalous response region.

There are many types of high-excitation density effects in the bulk which could increase either the lifetime or mobility. Lifetime lengthening from saturation of a volume distribution of recombination centers is one possibility. Such a model, however, would require the density of such centers to be about  $I\tau/h\nu l \approx 10^8 \text{ cm}^{-3}$  ( $l$ =diffusion length), an unrealistically low value. Another possibility is a mobility change caused by a change in carrier type under high excitation, an effect observed in Ge,<sup>19</sup> Si,<sup>20</sup> and GaAs.<sup>20,21</sup> The increase in mobility from this effect cannot be larger than the ratio of electron and hole mobilities (about 2 in GaP) and so cannot explain an increase as large as 100 found at  $77^\circ\text{K}$  (Fig. 2). Furthermore, the high-resistivity whiskers are *n* type in the dark. Another often observed mobility change resulting from optical excitation is caused by a reduction of ionized impurity scattering from their neutralization by photoexcited carriers. This effect has been observed in<sup>22</sup> Ge and in Si, CdS, and GaAs,<sup>20</sup> but gives only a factor of about 4 change and so cannot account for the anomalous response seen here.

An increase in mobility could also result from a reduction in trapping. In the indirect-transition region the drift mobility might be greatly reduced because of trapping while the higher excitation density resulting from the small absorption depth in the direct-transition region could saturate the traps, thus restoring the normal mobility. The number of traps which could be saturated is about  $10^8 \text{ cm}^{-3}$  just as calculated above for recombination centers. This number, however, is a little more reasonable as a possible trap density. Since the reduction in mobility from trapping would be greater at lower temperatures, the anomalous response caused by the restoration of the normal mobility would be greatest at low temperatures. The observations show this effect.

Though this last model must remain a possible explanation, a more likely one is that this anomalous response arises from the same origin as the large changes (factors of 10 to 100) in Hall mobility observed to occur under changes in illumination level in very-high-resis-

<sup>19</sup> W. W. Tyler and R. Newman, *Phys. Rev.* **98**, 961 (1955).

<sup>20</sup> R. H. Bube, H. E. MacDonald, and J. Blanc, *Phys. Chem. Solids* **22**, 173 (1961).

<sup>21</sup> R. H. Bube and H. E. MacDonald, *Phys. Rev.* **128**, 2071 (1962).

<sup>22</sup> W. W. Tyler and H. H. Woodbury, *Phys. Rev.* **102**, 647 (1956).

tivity crystals of InP,<sup>20</sup> CdSe,<sup>20</sup> and GaAs.<sup>23</sup> The mobility of these materials is anomalously low when in the dark and is believed limited by scattering from space-charge layers surrounding inhomogeneous distributions of deep donors or acceptors or other gross defects.<sup>23,24</sup> Incident light creates carriers which de-ionize the defects, remove the space charge layers, and allow the mobility to increase to a normal value. According to this model we have an anomalously low-mobility  $\mu_A$  in the normal response region (indirect-transition absorption region) and a normal mobility  $\mu_N$  in the anomalously high-response region (direct-transition absorption region).

Gross defect or Weisberg scattering<sup>24</sup> gives rise to an additional mobility  $\mu_W$  which combines with the other mobilities according to  $\mu_A^{-1} = \mu_N^{-1} + \mu_W^{-1}$ . Rearranging this yields  $\Delta\mu/\mu_A = \mu_N/\mu_W$ , where  $\Delta\mu = \mu_N - \mu_A$ . Relative values of  $\Delta\mu/\mu_A$  for different temperatures can be obtained from Figs. 1, 2, and 3 by subtracting the normal response from the anomalous response and dividing by the normal response. This gives values normalized to that at 296°K of 1,  $2.4 \pm 0.9$ , and  $9.9 \pm 3.5$  for 296°, 195°, and 77°K.

The Weisberg mobility<sup>24</sup> has a temperature dependence of  $n^{1/3}T^{-5/6}$ , where  $n$  is the free-carrier concentration. The normal mobility  $\mu_N$  is limited by a combination of polar scattering and ionized-impurity scattering and changes by factors between  $\frac{1}{2}$  and 4 between 296° and 77°K depending on the amount of ionized impurity scattering.<sup>25</sup> If the normal mobility is taken as constant between 296° and 77°K (Hall effect measurements could not be made because of the minute size of the whiskers), then  $\Delta\mu/\mu_N \sim T^{5/6}n^{-1/3}$ . This gives relative values of 1, 1.45, and 10.7 at 296°, 195°, and 77°K, which are in qualitative agreement with the experimental numbers quoted above. Further work will be necessary to prove whether this mechanism of mobility change is operative in GaP.

#### PHOTOCONDUCTIVE LIFETIME

The photoconductive lifetime of a high-resistivity whisker at 296°K (crystal H-15, Fig. 2) was found by the following procedure: The incident light intensity  $I_0$  at frequency  $\nu$  and the resultant photovoltage  $\Delta V_L$  across a resistance  $R_L$  (which was small compared to the whisker resistance) in series with the whisker were measured. In the volume absorption region the lifetime  $\tau$  is easily shown to be

$$\tau = h\nu b \Delta V_L / V_0 R_L I_A a e \mu, \quad (3)$$

where  $b$  is the length of the whisker,  $a$  the width of one of its three similar faces,  $\mu$  the drift mobility of the

<sup>23</sup> R. H. Bube and H. E. MacDonald, Phys. Rev. **128**, 2062 (1962).

<sup>24</sup> L. R. Weisberg, J. Appl. Phys. **33**, 1817 (1962).

<sup>25</sup> C. J. Frosch, M. Gershenson, and D. F. Gibbs, Symposium on Preparation of Single Crystals of the III-V Compounds, Battelle Memorial Institute, Columbus, 1959 (unpublished).

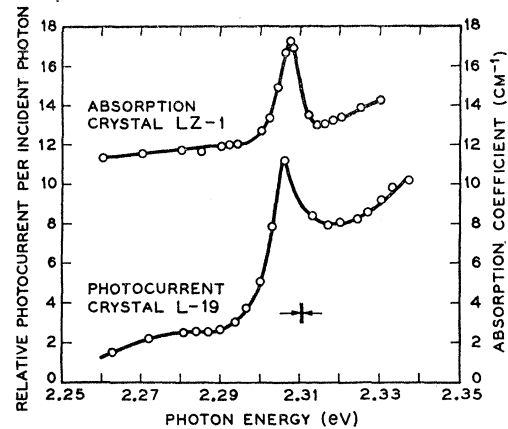


FIG. 8. Photoconductive spectrum at 77°K of an *n*-type, low-resistivity ( $0.2 \Omega\text{-cm}$  at 296°K), sulfur-doped GaP whisker in the region of absorption which produces excitons bound to neutral sulfur donors. An absorption spectrum at 77°K of a zone-refined, sulfur-doped crystal ( $0.8 \Omega\text{-cm}$  at 296°K) is also shown.

majority carrier,  $V_0$  the voltage applied to the crystal,  $I_A$  the absorbed light intensity given by Eq. (1), and  $e$  the electron charge. Measurements yielded  $I_0 = 1.1 \times 10^{-5} \text{ W/cm}^2$  at  $h\nu/e = 2.374 \text{ V}$ ,  $\Delta V_L = 1.6 \times 10^{-5} \text{ V}$ ,  $R_L = 5 \times 10^6 \Omega$ ,  $V_0 = 10^8 \text{ V}$ ,  $a = 5.4 \times 10^{-3} \text{ cm}$ , and  $b = 0.122 \text{ cm}$ . For  $\alpha = 2 \times 10^3 \text{ cm}^{-1}$  and  $R = 0.328$ ,  $I_A = 0.484 I_0$ . Therefore,  $\tau\mu = 3.0 \times 10^{-8} \text{ cm}^2/\text{V}$ . Following the reasoning of the last section we take  $\mu \approx 100 \text{ cm}^2/\text{V-sec}$ , the normal lattice mobility, at the direct-exciton peak, and so take  $\mu \approx 10 \text{ cm}^2/\text{V-sec}$  at  $h\nu = 2.374 \text{ eV}$ . Hence,  $\tau = 3 \times 10^{-9} \text{ sec}$ . Being a photoconductive lifetime, it is a majority carrier lifetime. The only measured lifetime in GaP to which it can be compared is a  $10^{-10}$ -sec electron minority carrier lifetime measured in a GaP surface-barrier junction.<sup>26</sup>

#### PHOTOCONDUCTIVITY FROM BOUND EXCITON ABSORPTION

In the photoconductivity spectra of low-resistivity sulfur-doped whiskers, a peak is invariably seen superposed on the indirect edge. Such a peak is seen in Fig. 7. Its width in that figure is resolution limited. Figure 8 shows the peak as it appears with the higher resolution of a grating instrument. It occurs at a photon energy of 2.306 eV, has a width of 0.007 eV and has a somewhat asymmetric shape.

Also shown in Fig. 8 is an absorption spectrum of a sulfur-doped crystal produced by the floating zone technique. An absorption line is seen at 2.307 eV with a width of 0.0055 eV. This line has been identified as due to the formation of an exciton bound to a neutral donor<sup>27</sup> found to be the sulfur atom.<sup>3</sup> It has been observed to shift as much as 0.002 eV in different samples,

<sup>26</sup> R. A. Logan and A. G. Chynoweth, J. Appl. Phys. **33**, 1649 (1962).

<sup>27</sup> D. G. Thomas, M. Gershenson, and J. J. Hopfield, Phys. Rev. **131**, 2397 (1963).

due apparently to crystal strain. Its width can also vary by a comparable amount.

We conclude from this comparison that the peak at 2.306 eV in the photoconductivity spectrum arises from absorption of a photon to form an exciton bound to a neutral sulfur atom with the subsequent dissociation of this complex into a free electron and free hole. Photoconductivity resulting from absorption in a similar type of complex in CdS and CdSe has recently been reported.<sup>28</sup>

It is of interest to inquire into the mechanism that dissociates this neutral, immobile complex into current carriers. Only two interactions seem possible: thermal processes (phonon impact) and free electron or hole impact. Though the latter process could contribute at the high electric fields applied to the whiskers ( $10^4$  V/cm), the former is believed to be the major cause of dissociation. This can be shown using a simple model. Let the binding energy of an electron and hole to a neutral sulfur atom with respect to a free electron and hole be  $E_B$ . Let the density of conduction band states be  $N_C$ , of valence band states  $N_V$ , of bound exciton states  $N_{BX}$  (equal to four times the density of neutral sulfur atoms  $N_S$  because of the spin degeneracy), of free electrons or holes created by the absorption of light  $\Delta$ , of free holes  $p = \Delta$ , of free electrons under no illumination  $n_0$ , of free electrons under illumination  $n = n_0 + \Delta$ , and of excitons bound to neutral sulfur atoms  $n_{bx}$ . Assume  $n_{bx} \ll N_{BX}$ ,  $n \ll N_C$ , and  $p \ll N_V$ . At thermal equilibrium a mass action law of the form

$$(np/n_{bx}) = (N_C N_V / N_{BX}) e^{E_B/kT} \quad (4)$$

results. For this experiment  $E_B = 0.012$  eV,  $T = 77^\circ\text{K}$ ,  $N_S = 1.5 \times 10^{18} \text{ cm}^{-3}$ ,  $N_C = 2.8 \times 10^{18} \text{ cm}^{-3}$  (corresponding to a density-of-states effective-mass ratio for electrons of 0.9) and  $N_V = 1.2 \times 10^{18} \text{ cm}^{-3}$  (corresponding to a density-of-states effective-mass ratio for holes of 0.5), and  $n_0 = 1.4 \times 10^{15} \text{ cm}^{-3}$ . From the measured illumination intensity and the lifetime found in the last section we have  $\Delta + n_{bx} \approx 1.8 \times 10^7 \text{ cm}^{-3}$ . Thus,  $n_{bx}/\Delta \approx n_0 N_{BX} \exp(E_B/kT) / N_C N_V = 0.016$ . We conclude that under the conditions of this experiment nearly all the bound excitons formed by absorption of light are ionized by thermal processes to produce current carriers. This conclusion is contrary to that of Gross and Novikov.<sup>17</sup>

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<sup>28</sup> Y. S. Park and D. C. Reynolds, Phys. Rev. **132**, 2450 (1963).

#### APPENDIX

An estimate of the direct exciton binding energy  $E_x$  can be obtained from the hydrogenic model which predicts

$$E_x = \mu \epsilon^4 / 2 \hbar^2 \epsilon^2 \quad (5)$$

with

$$\mu^{-1} = m_e^{-1} + m_h^{-1}, \quad (6)$$

where  $m_e$  and  $m_h$  are the electron and hole effective masses,  $\epsilon$  the dielectric constant (taken as<sup>29</sup> 10.18),  $e$  the electron charge, and  $\hbar$  Planck's constant over  $2\pi$ . The electron and light hole effective masses at  $\mathbf{k}=0$  in units of the free-electron mass  $m_0$  are given by

$$\frac{1}{m_e^*} = 1 + K \left( \frac{2}{E_G} + \frac{1}{E_G + \Delta} \right) \quad (7)$$

and

$$1/m_h^* = 2K/E_G - 1 \quad (8)$$

by Kane's theory.<sup>30</sup> Here  $E_G$  is the energy gap at  $\mathbf{k}=0$ ,  $\Delta$  the spin-orbit splitting of the valence band at  $\mathbf{k}=0$  and  $K$  is a constant. Ehrenreich has suggested that  $K$  should be nearly the same for all direct gap, group III-V semiconductors.<sup>31</sup> From data on InSb, InAs, InP, GaAs, and GaSb<sup>32</sup>  $K$  is found to be  $6.4 \pm 0.5$  eV. Assuming Eqs. (7) and (8) to hold for the direct gap in GaP, we get  $m_e^* = 0.13$  and  $m_h^* = 0.29$  by using  $E_G = 2.9$  eV and  $\Delta = 0.127$  eV.<sup>33</sup> Considering only the interaction with the lowest lying conduction band at  $\mathbf{k}=0$  as used to obtain Eqs. (7) and (8),<sup>30</sup> the heavy hole mass is given as unity. This result is less accurate than those for the other masses. The hole mass needed in Eq. (6) is a complex combination<sup>34</sup> of the light and heavy hole masses. However, if we use just the light hole mass in Eq. (6), we find  $\mu = 0.094 m_0$  and  $E_x = 0.013$  eV. Inclusion of the heavy hole mass can only raise  $E_x$ . On the other hand,  $E_x$  is most likely less than the *indirect* free-exciton binding energy which was found to be at most 0.012 eV.<sup>3,35</sup> On the basis of these several considerations, we estimate  $E_x = 0.013$  eV.

<sup>29</sup> D. A. Kleinman and W. G. Spitzer, Phys. Rev. **118**, 110 (1960).

<sup>30</sup> E. O. Kane, Phys. Chem. Solids **1**, 249 (1957).

<sup>31</sup> H. Ehrenreich, J. Appl. Phys. Suppl. **32**, 2155 (1961).

<sup>32</sup> T. S. Moss and A. K. Walton, Physica **25**, 1142 (1959).

<sup>33</sup> J. W. Hodby, Proc. Phys. Soc. (London) **82**, 324 (1963).

<sup>34</sup> T. P. McLean and R. Loudon, Phys. Chem. Solids **13**, 1 (1960).

<sup>35</sup> If, in the work of Ref. 3, the additional absorption beginning at 0.007 to 0.012 eV above the threshold for indirect free-exciton absorption is interpreted as creation of an exciton in its first excited state, rather than creation of an electron-hole pair, then the indirect free exciton would have a binding energy between 0.009 and 0.016 eV. (The indirect energy gap at 0°K found from that work would be increased correspondingly to 2.328 eV.)