

# Optical Absorption Due to Excitation of Electrons Bound to Si and S in GaP

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Infrared transmission measurements of GaP with S or Si donor impurities at liquid-helium temperature reveal absorption lines due to excitation of the donor electron. Strong absorption peaks corresponding to the  $1s \rightarrow 2p_{\pm}$  transition are observed, and their spectral positions are used to determine optical ionization energies of 104.2 and 82.5 meV ( $\pm 0.3$  meV), respectively, for S and Si donors in GaP. A fitting of Faulkner's effective-mass calculation for donor states to the observed levels yields the effective masses of the conduction band:  $m_1 = (0.191 \pm 0.005)m_0$  and  $m_{11} = (1.7 \pm 0.2)m_0$ . The  $p$ -like final states observed in these measurements are found to differ significantly in binding energy from the excited donor-electron states observed in the "two-electron" recombination of the exciton bound to neutral sulfur in GaP.

## I. INTRODUCTION

THE present paper reports the first observation of optical absorption due to the excitation of bound impurity electrons in gallium phosphide (GaP). Previous studies of single impurity states in GaP include a study of (a) the oxygen donor<sup>1</sup> by the method of luminescence excitation, (b) zinc and magnesium acceptors<sup>2</sup> by Raman scattering, and (c) sulfur, selenium, and tellurium donors<sup>3</sup> by means of "two-electron transitions" in the recombination luminescence of excitons bound to the neutral donors. All of these methods, especially the last, include possibilities for ambiguous interpretation of the data either because of the complexity of the process observed or because of lack of previous theoretical work to base the interpretation upon. Extensive investigations of donors and acceptors in silicon and germanium have been carried out by optical absorption.<sup>4-8</sup> In the case of donors in silicon and germanium, the effective-mass (EM) theory<sup>9,10</sup> has been found to describe the excited states very well. More recently, an extensive study of optical absorption by Group VI donors in aluminum antimonide (AlSb), together with effective-mass calculations for the observed energy levels, has been carried out by Ahlburn and Ramdas.<sup>11</sup> For AlSb, reasonable agreement between EM calculations and observed donor excited-state energies was found, although a definite species dependence was noted. In the case of GaP donors there

is no evidence of species dependence of donor excited states. Thus it is expected that the EM theory will describe the excited-state energies of donors in GaP quite well. The absorption spectra, then, together with EM calculations for donors in GaP by Kasami<sup>12</sup> and Faulkner<sup>13</sup> and extensive prior work on donor-acceptor pair spectra, yield revised values of impurity ionization energies in GaP. The donor ionization energies thus obtained are about 2 meV higher, and the acceptor energies about 2 meV lower, than the latest values tabulated by Dean *et al.*<sup>14</sup> The accuracy of the present values is determined primarily by the accuracy with which the EM theory describes donor excited states. As will be seen, the EM theory should describe excited states of donors in GaP quite well. The previous values of ionization energies relied heavily on a quantitative interpretation of the "two-electron" spectra for which a new interpretation is proposed in the present paper. The acceptor binding energies given here are determined from the present donor ionization energies and data on pair spectra presented by Dean *et al.*<sup>14</sup> and thus rely, in addition, on an accurate knowledge of the energy gap.

## II. EXPERIMENTAL

The sulfur-doped sample of GaP (No. 389) was vapor-grown on a GaP substrate. Details of the properties of this sample have been published by Taylor *et al.*<sup>15</sup> It had a carrier concentration of  $3.0 \times 10^{16}$  cm<sup>-3</sup> and mobility of 187 cm<sup>2</sup>/V sec at 300°K. No evidence of impurities other than sulfur was found in photoluminescence studies of this sample. The silicon doped GaP was solution grown by a method described by Plaskett *et al.*<sup>16</sup> It had a room-temperature carrier concentration of  $2 \times 10^{17}$  cm<sup>-3</sup> and mobility of 134 cm<sup>2</sup>/V

<sup>1</sup> P. J. Dean and C. H. Henry, *Phys. Rev.* **176**, 928 (1968).

<sup>2</sup> C. H. Henry, J. J. Hopfield, and L. C. Luther, *Phys. Rev. Letters* **18**, 1178 (1966).

<sup>3</sup> P. J. Dean, J. D. Cuthbert, D. G. Thomas, and R. T. Lynch, *Phys. Rev. Letters* **18**, 122 (1967).

<sup>4</sup> R. L. Aggarwal and A. K. Ramdas, *Phys. Rev.* **137**, A602 (1965); **140**, A1246 (1965).

<sup>5</sup> A. Onton, P. Fisher, and A. K. Ramdas, *Phys. Rev.* **163**, 686 (1967).

<sup>6</sup> R. L. Aggarwal, P. Fisher, V. Mourzine, and A. K. Ramdas, *Phys. Rev.* **138**, A882 (1965).

<sup>7</sup> J. H. Reuszer and P. Fisher, *Phys. Rev.* **135**, A1125 (1964); **140**, A245 (1965).

<sup>8</sup> R. L. Jones and P. Fisher, *J. Phys. Chem. Solids* **26**, 1125 (1965).

<sup>9</sup> W. Kohn and J. M. Luttinger, *Phys. Rev.* **98**, 915 (1955).

<sup>10</sup> W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957) Vol. 5, p. 257.

<sup>11</sup> B. T. Ahlburn and A. K. Ramdas, *Phys. Rev.* **167**, 717 (1968).

<sup>12</sup> A. Kasami, *J. Phys. Soc. Japan* **24**, 551 (1968).

<sup>13</sup> R. A. Faulkner, *Phys. Rev.* (to be published). He has performed EM calculations of the first nine  $s$ -like and first eighteen  $p$ -like "hydrogenic" states. The author would like to thank Dr. Faulkner for providing him with these results prior to their appearance in the literature.

<sup>14</sup> P. J. Dean, C. J. Frosch, and C. H. Henry, *J. Appl. Phys.* **39**, 5631 (1968).

<sup>15</sup> R. C. Taylor, J. F. Woods, and M. R. Lorenz, *J. Appl. Phys.* **39**, 5404 (1968).

<sup>16</sup> T. S. Plaskett, S. E. Blum, and L. M. Foster, *J. Electrochem. Soc.* **114**, 1303 (1967).

sec. The sulfur and silicon samples used had thicknesses of 0.022 and 0.013 cm, respectively.

The measurements were made using a Perkin-Elmer model 99-G double-pass monochromator together with a Reeder thermocouple detector. The samples were mounted in a stress-free manner on a brass cold finger which was cooled by contact with a liquid-helium bath. Atmospheric absorption was eliminated by flushing the spectrometer with nitrogen gas.

The data were analyzed assuming a reflection coefficient  $R=0.25$  for the sample.<sup>17,18</sup>

### III. EXPERIMENTAL RESULTS AND DISCUSSION

The absorption spectrum of S doped GaP in the 59–108-meV range of incident photon energy is given in Fig. 1. The spectrum is shown with the sample at about 15, 80, or 300°K. The last two are displaced upwards by 30 and 60  $\text{cm}^{-1}$ , respectively, for graphic clarity. Absorption lines believed to be due to donor-electron excitation in the material are labeled with the encircled numbers 2–6. The lines proposed as electron excitation lines have been chosen on the basis of their temperature dependence. The electronic absorption lines are expected to have a strong temperature dependence in the 15–300°K range because of thermal ionization of donors as well as excited-state lifetime broadening at the higher temperatures. This expected behavior is exhibited by lines 2–6. Absorption lines due to excitation of lattice vibrational modes or local modes shift slightly to lower energy with increasing temperature. However, except for a slight broadening, they remain approximately constant in absorption cross section. Further, it has been quite helpful to refer to the study of vibra-

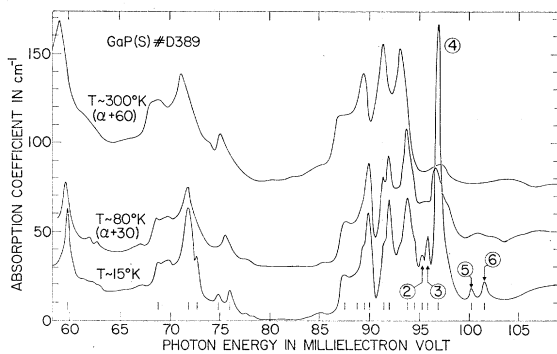


FIG. 1. Excitation spectra of sulfur donor in GaP. The electronic transitions are labeled by encircled numbers. The other absorption lines result from excitation of vibrational modes. The positions of the lines marked along the lower horizontal axis are given in Table I. The figure gives the spectrum with sample temperatures of about 15, 80, and 300°K. The last two curves have been displaced upward by 30 and 60  $\text{cm}^{-1}$ , respectively. The room-temperature carrier concentration is  $3 \times 10^{16} \text{ cm}^{-3}$ .

<sup>17</sup> W. L. Bond, J. Appl. Phys. **36**, 1674 (1965).

<sup>18</sup> A. N. Pikhtin and D. A. Yas'kov, Fiz. Tverd. Tela **9**, 145 (1967) [English transl.: Soviet Phys.—Solid State **9**, 107 (1967)].

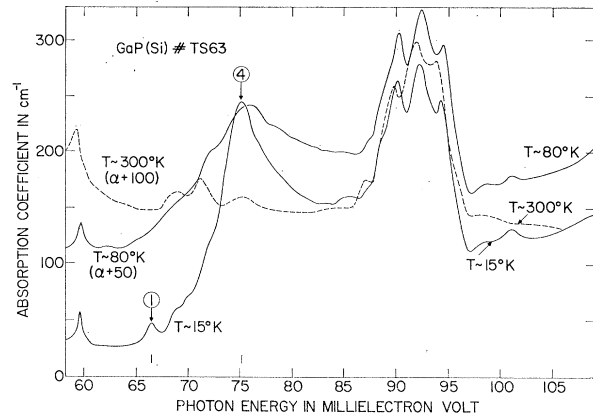


FIG. 2. Excitation spectra of silicon donor in GaP. The electronic transitions are denoted by the encircled numbers 1 and 4. The other absorption lines result from excitation of vibrational modes. The positions of the lines marked along the lower horizontal axis are given in Table I. The figure gives the spectrum with sample temperatures of about 15, 80, and 300°K. The last two curves have been displaced upward by 50 and 100  $\text{cm}^{-1}$ , respectively. The room-temperature carrier concentration is  $2 \times 10^{17} \text{ cm}^{-3}$ .

tional modes of defects in GaP by Spitzer *et al.*<sup>19</sup> to identify lattice and vibrational modes observed in the present investigation.

Absorption spectra of *n*-type Si-doped GaP are given in Fig. 2 for 15, 80, or 300°K sample temperatures. In this sample the net *n*-type characteristics of the material are believed to be due to Si substituting for Ga in the GaP lattice. Absorption believed to be due to excitation of the Si-donor electron is labeled by the encircled numbers 1 and 4 in the figure. Many of the vibrational modes observed in Fig. 1 are observed here, but with seemingly much poorer resolution. It is believed that the apparent decrease in resolution, as well as changes in absorption cross section of the prominent lattice modes from those observed in Fig. 1, are caused partly by large uncertainties in the calculation of absorption coefficient, because of the small percent transmission (1 to 2%) in the high-absorption regions shown in Fig. 2. The reason for the broadness of the Si-donor excitation line 4 is not known. It may be due partly to the large Si content of the material, which may give rise to excited-state banding. However, similar samples with  $n(\text{Si})$  in the  $3\text{--}8 \times 10^{16} \text{ cm}^{-3}$  range did not reveal a sharp line 4. Experimental difficulties alone cannot account for the spectral breadth of the observed line.

The spectral positions, at  $\sim 15^\circ\text{K}$ , of the neutral-donor excitation lines of Si and S and some prominent lines resulting from excitation of vibrational modes are given in Table I. The vibrational-mode lines will not be discussed in this paper. The electronic transitions are indicated by a "Line Number," and proposed assignments for the transitions are given. It is expected that

<sup>19</sup> W. G. Spitzer, W. Allred, S. E. Blum, and R. J. Chicotka, J. Appl. Phys. **40**, 2589 (1969).

TABLE I. Positions of absorption lines in meV.<sup>a</sup>

Line No.	GaP(S)	GaP(Si)	Assignment
1(Si)	59.80	66.48	$1s(T_2) \rightarrow 2p_0$
	68.92		
	71.73		
	72.65		
	74.88		
4(Si)	75.95	75.2	$1s(T_2) \rightarrow 2p_{\pm}$
	87.3		
	88.8		
	89.5		
	90.00		
	91.4		
	92.04		
	93.85		
	94.4		
	95.32		
	95.87		
2(S)	95.32		
3(S)	95.87		$1s(A_1) \rightarrow 3p_0$
4(S)	96.86		$1s(A_1) \rightarrow 2p_{\pm}$
5(S)	100.27		$1s(A_1) \rightarrow 3p_{\pm}$
6(S)	101.56		$1s(A_1) \rightarrow 4p_{\pm}$

<sup>a</sup> The lines recorded are those indicated by tick marks along the lower horizontal axes of Figs. 1 and 2. The positions observed at 15°K only are given. Estimated uncertainty is  $\pm 0.05$  meV, unless significant figures are given.

the ground state of the sulfur donor will be split by valley-orbit interaction in a manner similar to that determined for Group-V donors in silicon.<sup>20</sup> Thus the lowest ground-state level of sulfur donor is expected to be the symmetric electron state transforming according to the irreducible representation  $A_1$  of  $T_d$ ; the higher  $1s(E)$  state is not observed in the present experiments. For a silicon donor in GaP, however, Morgan<sup>21</sup> has shown that the symmetry of the ground state will be  $T_2$ . The degeneracy of this state cannot be resolved by an interaction which has the symmetry of the impurity site. This site dependence of donor-state symmetry results from the fact that the electron Bloch functions at the conduction-band minima at Ga sites have nodes, whereas at P sites they are at their maximum. The final states of the transitions assigned in Table I have been proposed on the basis of the assumption that the strongest line is the  $1s \rightarrow 2p_{\pm}$  transition. This has been found to be true for all previous studies of absorption due to donor-electron excitation.<sup>4,6,7</sup> Moreover, the theoretical matrix element for this  $1s \rightarrow np$  transition is the strongest. The other observed transitions are then assigned by correlation with theoretically expected line spacings calculated on the basis of the EM theory.<sup>13</sup> Line 1 of GaP(S), the  $1s(A_1) \rightarrow 2p_0$  transition, is expected to lie under the lattice bands near 88 meV and, thus, is not observed. No identification of line 2 has

<sup>20</sup> A three-valley model for the GaP conduction band is assumed in this study. This merely eliminates the  $1s(T_2)$  state that exists for a six-valley conduction band as in silicon. The group theoretical representation notation used in this paper is as defined by V. Heine, *Group Theory in Quantum Mechanics* (The Macmillan Co., New York, 1964). We note that this notation is different than defined in Refs. 9 and 10 for the irreducible representations  $T_1$  and  $T_2$ .

<sup>21</sup> T. N. Morgan, Phys. Rev. Letters **21**, 819 (1968).

been possible; it can not be ruled out that it is not due to an absorption by a weak vibrational mode which disappears in the broad electronic excitation lines at higher temperatures.

The differences in binding energy of some of the donor states calculated in the EM approximation and corresponding energies observed experimentally are given in Table II. The EM binding energies have been taken from the paper by Faulkner,<sup>13</sup> the effective-mass anisotropy factor  $\gamma$  having been determined on the basis of the ratio of the  $2p_{\pm} - 2p_0$  to  $3p_{\pm} - 2p_{\pm}$  energy differences. It is evident in Table II that by a suitable choice of parameters the observed energy levels can be described by Faulkner's<sup>13</sup> EM calculations of donor-electron energy levels. The adjustable parameters in the theoretical results,<sup>13</sup>  $\gamma$ , the effective-mass anisotropy ( $m_{\perp}/m_{\parallel}$ ), and  $\epsilon_0$  the ground-state energy in the limit  $\gamma \rightarrow 1$ , were adjusted to give an optimum fit for the observed spacings of the  $2p_0$ ,  $2p_{\pm}$ , and  $3p_{\pm}$  levels. The resulting fit between theoretical and experimental results is within experimental uncertainty except for the  $2p_{\pm} - 3p_0$  spacing. In this case, however, the experimental result lies well within the error limits of the EM calculation. The error limits on the EM results were estimated on the basis of the experimental uncertainty of the  $2p_{\pm} - 2p_0$   $3p_{\pm} - 2p_{\pm}$  energy differences used in the determination of  $\gamma$ .

The correlation between the donor-electron states observed experimentally and calculated by Faulkner<sup>13</sup> is good enough to permit an estimate of the conduction-band effective masses. If the dielectric constant is taken as<sup>24</sup> 11.1, the value of  $\epsilon_0$  for optimum fit between experiment and theory implies  $m_{\perp} = (0.191 \pm 0.005)m_0$ . Then, using  $\gamma = 0.11 \pm 0.01$  as determined from a fit between experiment and theory,  $m_{\parallel} = (1.7 \pm 0.2)m_0$ . These values of effective mass imply a central value of  $m_F^* = 0.33m_0$ , the Faraday-rotation effective mass,

TABLE II. Energies of donor states (meV).

States	EM theory <sup>a</sup>	GaP(S)	GaP(Si)
$2p_{\pm} - 2p_0$	$8.7 \pm 0.6$		$8.7 \pm 0.2$
$2p_{\pm} - 3p_0$	$0.8 \pm 0.4$	$0.99 \pm 0.1$	
$4p_0 - 2p_{\pm}$	$2.3 \pm 0.3$		
$3p_{\pm} - 2p_{\pm}$	$3.4 \pm 0.1$	$3.41 \pm 0.1$	
$4p_{\pm} - 2p_{\pm}$	$4.6 \pm 0.1$	$4.70 \pm 0.1$	
$\epsilon_I - 2p_{\pm}$	$7.3 \pm 0.1$	$\epsilon_I = 104.2^b$	$\epsilon_I = 82.5^b$

<sup>a</sup> Determined from the calculations of Faulkner (Ref. 13). The effective-mass ratio  $\gamma = m_{\perp}/m_{\parallel}$  was determined to be  $0.11 \pm 0.01$  from a fit of the experimentally observed ratio of  $(2p_{\pm} - 2p_0)/(3p_{\pm} - 2p_{\pm})$  splittings. The energy  $\epsilon_0$  [ $(m_{\perp}/m_0)/\kappa^2$  Rydbergs], where  $\kappa$  is the dielectric constant, was found to be 21.1 meV for an optimum fit with the data. This value of  $\epsilon_0$  is realized in a range [ $\kappa = 11.1$ ,  $(m_{\perp}/m_0) = 0.191$ ] - [ $\kappa = 11.4$ ,  $(m_{\perp}/m_0) = 0.202$ ]. The best independent values of these parameters are  $\kappa = 11.1$  (Ref. 24) and  $(m_{\perp}/m_0) = 0.202$  (determined from the Faraday-rotation effective mass of  $(0.35 \pm 0.1)m_0$  in Ref. 22. The EM  $1s$  ground-state binding energy obtained is 38.2 meV.

<sup>b</sup> Effective-mass binding energy of  $2p_{\pm}$  level plus observed energy of  $1s \rightarrow 2p_{\pm}$  transition. Assuming a total uncertainty of  $\pm 0.2$  meV in the EM binding energy, the uncertainty in the ionization energies is  $\pm 0.3$  meV.

<sup>24</sup> P. J. Dean, C. H. Henry, and C. J. Frosch, Phys. Rev. **168**, 812 (1968).

which agrees well with the value of  $m_p^* = (0.35 \pm 0.01)m_0$  determined by Moss *et al.*<sup>22</sup>

It is encouraging to note that the energy difference of the  $2p_{\pm}$  lines for S and Si, 21.7 meV, is, well within experimental error, the difference of the S and Si donor ionization energies given by Dean *et al.*<sup>14</sup> This observed lack of species dependence in the excited-state binding energy is essential to the validity of the EM theory in predicting donor-electron excited states in GaP and is well in accord with the same case for donors in Si.<sup>13</sup> Thus it is possible to calculate the ionization energies of the donors by adding the EM binding energy of the  $2p_{\pm}$  level to the experimentally observed energy of the  $1s \rightarrow 2p_{\pm}$  transition. The resulting ionization energies are 104.2 and 82.5 meV ( $\pm 0.3$  meV) for sulfur and silicon donors in GaP, respectively. The uncertainty in these figures is determined primarily by the uncertainty in the calculation for the EM binding energy of the  $2p_{\pm}$  excited state. On the basis of the differences in ionization energy observed in donor-acceptor pair line luminescence spectra,<sup>14,23</sup> and "two-electron" spectra,<sup>3</sup> the ionization energy calculated here for a sulfur donor immediately predicts ionization energies of  $102.8 \pm 0.6$  and  $89.4 \pm 0.6$  meV for selenium and tellurium donors in GaP. Acceptor binding energies can also be estimated by reference to pair spectra. Table III presents a summary of the ionization energies of acceptors and donors in GaP, obtained by using the sums of donor and acceptor ionization energies,  $(E_A + E_D)$ , given by Dean *et al.*<sup>14</sup> and the ionization energies for Si and S donors determined here.

The present results are not consistent with the original interpretation of the "two-electron" spectra.<sup>3</sup> Dean *et al.*<sup>3</sup> proposed that the lines in this spectrum result when the sulfur (selenium, tellurium) donor electron is left in an excited bound state as the exciton bound to the neutral donor recombines. Thus the energy difference between the zero-phonon no-interaction exciton recombination line  $S_0$  ( $Se_0$ ,  $Te_0$ ) and the lines of the two-electron spectrum should correspond to energies of excitation of the donor electron from the  $1s(A_1)$  level to various excited states. Although they noted a parity

TABLE III. Ionization energies of electronic impurities in GaP.<sup>a</sup>

Acceptor	$\epsilon_I$ (meV)	Donor	$\epsilon_I$ (meV)
Si	202 $\pm$ 2	S	104.2 $\pm$ 0.3
Cd	94 $\pm$ 2	Se	102.8 $\pm$ 0.6
Zn	61.5 $\pm$ 2	Te	89.4 $\pm$ 0.6
C	46 $\pm$ 2	Si	82.5 $\pm$ 0.3
		O	895 $\pm$ 3

<sup>a</sup> The ionization energies of Si and S donors determined here, expanded by means of values of  $(E_A + E_D)$  given by Dean *et al.* (Refs. 14 and 24).

<sup>22</sup> T. S. Moss, A. K. Walton, and B. Ellis, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and The Physical Society, London, 1962), p. 295.

<sup>23</sup> D. G. Thomas, M. Gershenson, and F. A. Trumbore, *Phys. Rev.* **133**, A269 (1964).

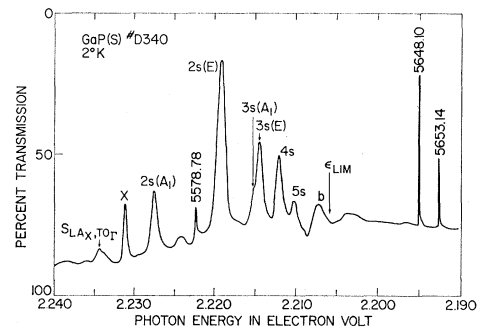


Fig. 3. Photoluminescence spectrum of sulfur-doped GaP in the region of the "two-electron" transitions. Plotted is the percent transmission of a photographic plate exposed to the luminescence. Three calibration lines from a rubidium spectral lamp with their wavelength marked in Å also appear in the trace. The "two-electron" lines are labeled according to the final state of the donor electron; these tentative assignments are discussed in the text. The origin of the line X is not known. The photoluminescence here is excited by the 4880 Å line of an argon-ion laser, and the emitted light was analyzed by a Bausch and Lomb 2-m spectrograph with a 1200-line/mm grating.

violation in their interpretation, Dean *et al.*<sup>3</sup> suggested that the lines of the two-electron spectrum corresponded to the excitation of the donor electron from the  $1s(A_1)$  level to various  $p$ -like excited states. This assignment was based primarily on the similarity of the two-electron spectrum (see Fig. 3 for the two-electron spectrum of sulfur in GaP) to the excitation spectra of donors in silicon.<sup>4,6</sup> However, no obvious correlation between the lines of the two-electron spectra and the excitation spectra reported here exists. Table IV presents a comparison of these two results. The binding energies of the final states observed in both cases are calculated using an ionization energy of 104.2 meV for the sulfur donor. Positions of the lines relative to the most prominent line in each of the spectra are also given. There are some approximate coincidences of binding energy or line spacings in this table. However, when all available facts, including relative intensities of lines in the two spectra, are considered, it becomes clear that no single energy-level scheme will describe both the spectra.

In view of the simplicity of the interpretation for the infrared donor excitation spectra ( $1s[A_1] \rightarrow np$  transitions), it is probable that the two-electron spectra require a new interpretation. Efforts in this direction have been credited to Faulkner.<sup>1,14,24</sup> The present results suggest that the excited states observed in the two-electron spectra are even parity states not observable in absorption measurements. In view of this, we concur on the basis of direct experimental evidence with the suggestion credited to Faulkner<sup>1</sup> that the final states of the prominent two-electron spectral lines are  $s$  like. A proposed set of assignments are given in Table IV and Fig. 3. The assignments reflect the fact that the excited  $s$ -like states would be expected to undergo a valley-orbit splitting similar to that of the

TABLE IV. Binding energies of excited states of sulfur donor in GaP.

"Two-electron" spectrum				Excitation spectrum		
Assignment <sup>a</sup>	Line positions (eV)	$\Delta^a$	B.E. <sup>b</sup>	B.E. <sup>b</sup>	$\Delta^a$	Assignment
$2s(A_1)[2p_0]$	2.2276	8.4	21.6	16.0	8.7	$2p_0$
$2s(E)[2p_{\pm}]$	2.2192		13.2			
$3s(A_1)[4p_0]$	2.2152	4.0	9.2	8.8	1.5	line 2
$3s(E)[3p_{\pm}]$	2.2144	4.8	8.4	8.3	1.0	$3p_0$
				7.3		$2p_{\pm}$
$4s[4p_{\pm}]$	2.2122	7.0	6.2	3.9	3.4	$3p_{\pm}$
$5s[5p_{\pm}]$	2.2103	8.9	4.3	2.6	4.7	$4p_{\pm}$
[b]	2.2077	11.5	1.7			
$\epsilon_{LM}^d$	2.2060	13.2	...	...	7.3	$\epsilon_I$

<sup>a</sup> Separation from  $2p_{\pm}$  or  $2s(E)$  line in meV.

<sup>b</sup> Experimental binding energy in meV.

<sup>c</sup> Assignment of Dean *et al.* (Ref. 3) is given in square brackets.

<sup>d</sup> Position of zero-phonon recombination line of exciton bound to S in GaP ("S<sub>0</sub>" line), 2.3102 eV at 2.0°K, minus  $\epsilon_I(S) = 104.2$  meV.

ground state except in magnitude.<sup>9</sup> On the basis of the quantum defect model proposed by Kohn and Luttinger,<sup>9</sup> the valley-orbit splitting of higher  $s$ -like levels can be scaled from the ground-state valley-orbit splitting.<sup>25</sup> Thus, a  $2s(A_1) - 2s(E)$  energy difference of about 7.4 meV due to the valley-orbit interaction can be expected for a sulfur donor; it is found to be 8.3 meV according to the proposed assignments of the "two-electron" transitions. For the higher  $s$ -like levels, the quantum-defect model predicts much larger valley-orbit splittings than are observed. This model would also predict a difference in the  $2s(A_1) - 2s(E)$  splitting for Te and S donors of about 1.3 meV; in fact, no species dependence at all is observable in data reported by Dean *et al.*<sup>3</sup> This lack of species dependence in the two-electron spectra implies that the EM theory describes excited donor states well (except for the valley-orbit splitting, of course)—thus encouraging the application of EM calculations to the states observed in infrared absorption, but complicating the assignment of the final states involved in the two-electron spectra. Moreover, it is puzzling that no  $1s(A_1) \rightarrow 1s(E)$  transition is observed in the two-electron spectra if transitions to other  $s$ -like levels are allowed. On the basis of the Raman scattering by donor electrons in silicon observed by Wright and Mooradian,<sup>26</sup> one would expect the  $1s(A_1) \rightarrow 1s(E)$  transition to be by far the strongest. Finally, using the same parameters that were determined for an optimum fit of the  $p$ -like levels of donors in GaP, Faulkner's<sup>13</sup> EM calculations yield binding energies of 11.9, 6.6, 4.8, and 4.0 meV for the  $2s$ ,  $3s$ ,  $4s$ , and  $5s$

<sup>25</sup> The valley-orbit splitting of the sulfur donor is assumed to be 66 meV, i.e., the ionization energy (104 meV) less the EM position of the ground state ( $1.81\epsilon_0 = 38$  meV; see Ref. 13).

<sup>26</sup> G. B. Wright and A. Mooradian, Phys. Rev. Letters **18**, 608 (1967).

excited states, respectively. These binding energies should be compared with the binding energies of the  $2s(E)$ ,  $3s(E)$ ,  $4s$ , and  $5s$  levels in Table IV. They are from 0.3 to 1.8 meV smaller than the experimentally determined binding energies. It is not unexpected for the observed levels to have a slightly larger binding energy than the calculation predicts. However, the fact that the difference between observed and calculated values does not go to zero monotonically as the principal quantum number increases is unexpected. No definite explanations of these difficulties in the interpretation of the two-electron spectra can be made at this time.

Finally, Dean and Henry<sup>1</sup> have observed that on the basis of their luminescence excitation spectra they could obtain an ionization energy of  $897 \pm 1$  meV for oxygen donors in GaP. They note that this value would be  $4 \pm 3$  meV higher than is obtained by Dean *et al.*<sup>14</sup> from donor-acceptor pair spectra involving oxygen donors. The former value for  $\epsilon_I(0)$ , however, is more consistent with the ionization energies given in Table III, obtained by use of the 104.2 meV ionization energy of sulfur donors determined here.

#### IV. CONCLUSIONS

The donor excitation spectra of Si and S in GaP have been observed. The observed transitions have been found to be consistent with effective-mass calculations of donor excited states in GaP. On the basis of the EM calculations and experimentally observed transitions, conduction-band effective masses,  $m_{\perp} = (0.191 \pm 0.005)m_0$ , and  $m_{\parallel} = (1.7 \pm 0.2)m_0$ , have been found, and ionization energies of  $82.5 \pm 0.3$  and  $104.2 \pm 0.3$  meV have been determined for Si and S donors in GaP. These ionization energies, in turn, lead to a revision of all previous determinations of impurity ionization energies in GaP.

The infrared transitions observed here are undoubtedly of the type  $1s \rightarrow np$ . As a result, because of discrepancies with the two-electron transitions, they suggest that the final states in the two-electron spectra are  $s$ -like excited states of the donor.

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