Spectroscopic Study of Tellurium Donors in GaP

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The $1s(A_1) \rightarrow 2p_0$ and $2p_{\pm}$ transitions in Te donors in GaP have been observed. Together with similar data for Si and S donors, Faulkner's effective-mass (EM) calculations yield an ionization energy of 89.8±0.3 meV for Te donors. Conduction-band effective masses consistent with all the data for these GaP donors are $m_{\perp} = (0.180 \pm 0.005)m_0$ and $m_{\parallel} = (1.5 \pm 0.2)m_0$. The effects of uniaxial stress on the "two-electron" transitions in the recombination of excitons bound to neutral Te donors in GaP are consistent with the final donor states observed being s-like with a valley-orbit splitting.

I. INTRODUCTION

INFRARED absorption due to excitation of electrons bound to tellurium donors in GaP and the "two-electron" transitions in the recombination radiation of excitons bound to neutral tellurium donors in GaP have been investigated at liquid-helium temperatures. This is the first time that infrared excitation spectra of Te donor in GaP have been reported or that two-electron spectra in GaP have been measured with uniaxial stress applied to the sample. The purpose of the present study has been to establish precisely the optical ionization energy of tellurium donors on the basis of infrared excitation spectra and effective-mass (EM) calculations. Besides being of interest by itself, this result is a valuable confirmation of a similar study of silicon and sulfur donors in GaP.[1] In this previous study,[1] conflicts of data and theoretical expectations appeared in the interpretation of the two-electron transitions involving sulfur donors in GaP. An equal objective of the present study has been to obtain precise binding energies and degeneracies of the final states observed in the two-electron transitions in order to provide a quantitative basis for a detailed theoretical understanding of the neutral-donor–bound-exciton system.

Two types of optical measurements have been utilized in this study: (1) infrared absorption and (2) photoluminescence in the "near-band-gap" region. Infrared absorption spectra yield the energy of excitation of a bound-charge carrier from its ground state to higher-lying bound states. Such spectra were first observed by Burstein *et al.*[2] for boron acceptors in silicon. The value of this technique in the study of electronic impurity level is exemplified by the work of the group at Purdue University.[3] In photoluminescence, spectral lines corresponding to bound-exciton recombination with the simultaneous excitation of the donor electron to one of its excited states provide the energies of a set of higher-lying donor energy levels not observed in infrared absorption. These two-electron transitions, observed in the radiative recombination spectra of excitons bound to neutral donors in GaP, were first reported by Dean *et al.*[4] Similar two-electron transitions involving the intra-ground-state excitation of the donor electron have been observed in the recombination photoluminescence of excitons bound to neutral donors in Si and Ge by Dean *et al.*[5]

The basis of theoretical understanding of electronic impurity states in semiconductors is the EM theory developed by Kohn[6] and Luttinger.[7] Recently, Faulkner[8] has made a precise calculation of the 27 lowest eigenvalues of the EM Hamiltonian for donors by the Rayleigh-Ritz method. He finds that these calculated eigenvalues represent the experimentally observed electronic energy levels of donors in Si and Ge[3] very well. It was found that the observed p-like levels of Si and S donors in GaP[1] also could be described very well in terms of Faulkner's results.[8] When these EM calculations are applied to a series of energy levels such as the excited states of donors, they provide very precise values for the binding energies of these levels as well as precise values of parameters entering into the calculation (dielectric constant and conduction-band effective masses).

II. VAPOR GROWTH AND ELECTRICAL PROPERTIES OF Te-DOPED GaP

The vapor-grown GaP crystals were prepared by a PCl_3 transport method as previously described.[9,10] The gallium source temperature was maintained at 900°C, the substrate temperature at 800°C, and the PCl_3

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[8] R. A. Faulkner, Phys. Rev. **184**, 713 (1969).
[9] R. C. Taylor, J. Electrochem. Soc. **116**, 383 (1969).
[10] R. C. Taylor, J. F. Woods, and M. R. Lorenz, J. Appl. Phys. **39**, 5404 (1968).

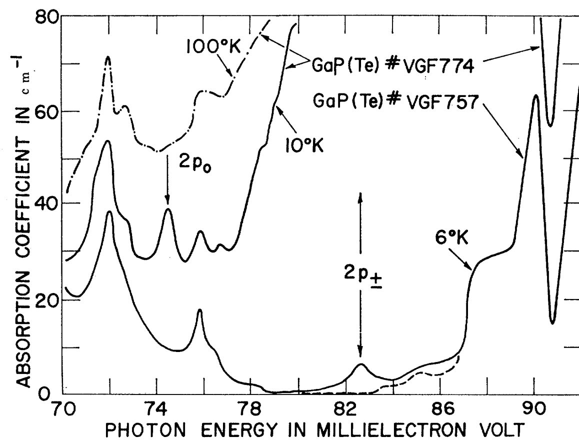

FIG. 1. Infrared absorption spectra of two samples of Te-doped GaP. The heavily doped sample No. VGF 774 shows the $1s(A_1) \to 2p_0$ transition clearly; the lightly doped sample No. VGF 757 shows the $1s(A_1) \to 2p_\pm$ transition clearly. The temperature dependence of the spectrum for VGF 774 exhibits the fact that the $1s(A_1) \to 2p_0$ transition vanishes rapidly with increased temperature, unlike the lattice or local vibrational mode absorption lines. The dashed curve near $\alpha = 0$ cm^{-1} is the absorption spectrum of a S-doped GaP sample No. D 389.

bubbler at −30°C. Total hydrogen flow was 100 cm^3/min of which 50 cm^3/min passed through the PCl_3 bubbler to give a PCl_3 flux of 1.2×10^{-3} mole/h. 40 cm^3/min were employed as a diluent gas stream and 10 cm^3/min passed over a Te pellet in the doping line. The Te pellet was held at a temperature (about 400°C) to give the desired doping level. The tellurium flux in run 757, as determined by pellet weight loss, was 1×10^{-7} mole/h as Te_2.

Vapor-grown and solution-grown (111)A GaP crystals were used as substrates for the Te-doped growths. The substrates were chemically polished with an H_2SO_4-H_2O_2 etch before introduction into the system. The (111)A orientation was used because of its previously observed property of rejecting donor impurities during vapor growth.[9] Thus, the unwanted sulfur impurity, which is commonly present in the vapor stream in very low concentrations, could be kept below the limit of detectability in the crystal. Te could then be introduced into the crystal at the desired level without the interference of sulfur in the spectra. Of course, Te also tends to be rejected on a (111)A face but this is compensated for by introducing a high Te flux into the system and assuming that the Te concentration in the crystal will be one to two orders of magnitude lower than in the vapor phase.

TABLE I. Energies of donor states in meV.

States	EM theory[a] (A)	(B)	Observed
$2p_\pm - 2p_0$	8.0	8.46	(A) 8.0, GaP(Te); (B) 8.4 GaP(Si)
$2p_\pm - 3p_0$	0.4	0.7	1.0, GaP(S)
$4p_0 - 2p_\pm$	2.5	2.3	
$3p_\pm - 2p_\pm$	3.4	3.4	3.4, GaP(S)
$4p_\pm - 2p_\pm$	4.6	4.6	4.7, GaP(S)
$\epsilon_I - 2p_\pm$	7.2	7.2	

[a] Determined from the calculations of Faulkner (Ref. 8). In column (A), the effective-mass ratio $\gamma = m_\perp/m_\parallel$ was determined to be 0.125 ± 0.01 on the basis of the experimentally observed ratio of $(2p_\pm - 2p_0)/(3p_\pm - 2p_\pm)$ energies of Te and S donors in GaP. In column (B), $\gamma = 0.117\pm0.01$ on the basis of Si and S donor data. The energy $\epsilon_0 = [(m_\perp/m_0)/\kappa^2 \text{ Ry}]$ is found to be 21.09 and 21.20 meV in the two cases, respectively; with $m_\perp = 0.180\ m_0$ and $\kappa = 10.75$.

The electrical properties of the crystals were measured by the Van der Pauw method. Sample VGF 757 was n type with a room-temperature carrier concentration of 4.1×10^{15} cm^{-3}. The Te concentration in this sample was apparently just slightly above that required to compensate the 10^{16}-cm^{-3}-deep acceptors normally found in (111)A face growth.[9] Sample VGF 774 was n type with a room-temperature carrier concentration of 1.4×10^{17} cm^{-3}.

III. OPTICAL MEASUREMENTS

The infrared measurements were made using a Perkin-Elmer model 99-G double-pass monochromator together with a Reeder thermocouple detector. The photoluminescence spectra were taken with a Bausch and Lomb 2-m spectrograph, the luminescence being excited by the 4880 Å line from an argon ion laser. The sample was maintained at liquid-helium temperatures during the measurements in a Janis Super Vari-Temp Dewar with IRTRAN 6 or fused-quartz cold windows, respectively. Atmospheric absorption in the infrared was eliminated by flushing the spectrometer with nitrogen gas. The infrared data were analyzed assuming a reflection coefficient of 0.25 for the sample.[11]

The samples were too thin to withstand sufficient uniaxial stress applied directly to the sample because of vibrations in the equipment. Thus, in uniaxial stress measurements, the samples were glued with grease into a copper jig designed so that uniaxial stress applied to the copper jig was transmitted to the sample as uniaxial stress.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Infrared Excitation Spectra

The infrared excitation spectra of tellurium donors in GaP are shown in Fig. 1 for two concentrations of Te impurities. The very strong $1s(A_1) \to 2p_\pm$ transition at 82.57 ± 0.05 meV is best observed in the lightly doped sample, VGF 757. The relatively weak $1s(A_1) \to 2p_0$ transition at 74.55 ± 0.05 meV is detectable only in the more heavily doped sample, VGF 774. Transitions involving other p-like excited states have not been observed, presumably because the necessary combination of impurity concentration and sample thickness have not been attained in the present vapor-growth series. Part of a spectrum of VGF 774 at 100°K is shown in Fig. 1 to demonstrate that the line $2p_0$

[11] W. L. Bond, J. Appl. Phys. **36**, 1674 (1965); A. N. Pikhtin and D. A. Yas'kov, Fiz. Tverd. Tela **9**, 145 (1967) [English transl.: Soviet Phys.—Solid State **9**, 107 (1967)].

disappears rapidly with increasing temperature as it should if it results from an electronic transition. A similar temperature dependence of the $2p_{\pm}$ line is evident in Fig. 2.

Also shown in Fig. 2 are the $2p_{\pm}$ line of Si donor and the absorption spectrum of sample D389 which was predominantly sulfur-doped. This last spectrum is part of a spectrum obtained in a previous study of Si and S donors in GaP.[1] It has now become evident that the absorption peak at 74.88 meV in D389 is due to excitation of electrons on Si donors from the ground state to the $2p_{\pm}$ level. This interpretation is borne out by the temperature dependence of the absorption spectrum given in that study.[1] There, on the basis of another sample, the $2p_{\pm}$ line was reported to be about 0.3 meV higher in energy than has been observed in all subsequent spectra of Si donors. It is clear that the position of the Si donor $2p_{\pm}$ line shown here is the correct one because of the higher purity of the host GaP. It is important to note in Fig. 2 that the observed Te $2p_0$ line is distinctly lower in energy than the Si $2p_{\pm}$ line because Si is apparently a parasitic impurity in the vapor grown GaP. The Si is believed to originate from the walls of the quartz-vapor transport system.

The quantitative results for the infrared donor excitation spectrum are summarized in Table I. Here, the experimentally observed energy spacings of various excited states are compared to spacings taken from the EM calculations of Faulkner[8] for two different values of the parameter $\gamma = m_{\perp}/m_{\parallel}$. The data for Si and S donors are taken from an earlier study[1] except for the data on the position of the Si donor $2p_{\pm}$ line. A small species dependence of the $2p_{\pm}-2p_0$ splitting is observed experimentally. This affects primarily the determination of the effective-mass ratio γ. The theoretical EM results in Table I are, thus, presented for two values of γ, determined from the $2p_{\pm}-2p_0$ splitting observed for (a) Te and (b) Si donors, respectively. It is clear in Table I that the EM theoretical spacings between the $2p_{\pm}$, $3p_{\pm}$, and $4p_{\pm}$ lines and the EM theoretical binding energy of the $2p_{\pm}$ level, $\epsilon_I - 2p_{\pm}$, are not affected significantly by the observed differences in the $2p_{\pm}-2p_0$ spacing for Si and Te donors. The fit of the $3p_0$ line by the EM theory has become worse with the new data.[12] In spite of the noted species dependence, all of the present infrared absorption lines can be assigned within experimental error by taking $\gamma = 0.12 \pm 0.01$ and $m_{\perp} = (0.180 \pm 0.005) m_0$. This implies $m_{\parallel} = (1.5 \pm 0.2) m_0$ and donor ionization energies $\epsilon_I = (82.1, 89.8, 104.1 \pm 0.3)$ meV for Si, Te, and S donors in GaP, respectively.

[12] In view of the marginal agreement between experimental and theoretical EM positions of the $3p_0$ level relative to the other p-like excited states and also the rather large absorption cross section of the line identified as the $1s \to 3p_0$ transition when compared to the approximate expected intensity $[I(3p_{\pm}) \times (I(2p_0)/I(2p_{\pm})]$, the assignment for this transition must be considered questionable. This does not affect any of the previous conclusions relating to donor ionization energies or conduction-band effective masses.

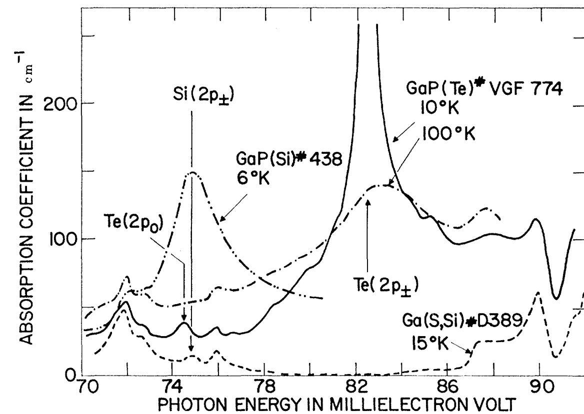

FIG. 2. Infrared absorption spectrum of Te-doped GaP No. VGF 774. The temperature dependence exhibits the expected behavior for the electronic transition $1s(A_1) \to 2p_{\pm}$. The spectrum of GaP(S,Si) No. D 389 is shown for a background reference. The spectrum of Si-doped GaP No. 438 is shown to distinguish between the Te donor $1s(A_1) \to 2p_0$ and Si donor $1s(T_2) \to 2p_{\pm}$ transitions.

B. Two-Electron Transitions in Exciton Recombination

The two-electron spectrum of Te donors in GaP is shown in Fig. 3. The lowest curve is taken with no externally applied stress on the sample. Above this curve are two spectra taken with the sample under uniaxial stress with the externally applied force along the [110] crystallographic direction. These spectra result when an exciton bound to a neutral donor recombines radiatively with the simultaneous excitation of the donor electron to an excited state of the donor. The first observation and identification of these transitions was made by Dean *et al.*[4] The experimentally observed positions of the two-electron lines for Te donors are given in Table II together with the experimental binding energies of the final states for both Te and S donors. The EM binding energies of some

TABLE II. Binding energies of excited states observed in two-electron spectra.

Assignment	GaP(Te) Line pos (±0.0001 eV)	GaP(Te) B. E.[a] (±0.1 meV)	GaP(S)[b] B. E.[a] (±0.1 meV)	EM theory[c] B. E. (meV) (A)	EM theory[c] B. E. (meV) (B)
$2s(A_1)$	2.2420	21.6	21.5		
$2s(E)$	2.2334	13.0	13.1	11.5	11.8
$3s(A_1)$	2.2304	10.0	9.1		
$3s(E)$	2.2288	8.4	8.3	6.3	6.5
$3d_0$	2.2265	6.1	6.1	4.6	4.7
$4s$	2.2251	4.7	4.2	3.9	4.0
b	2.2222	1.8	1.6		
b'	2.2218	1.4			
ϵ_{LIM} [d]	2.2204	0	0		

[a] Experimental binding energy in meV, error estimate is for relative values only.
[b] From Ref. 1.
[c] Determined from the calculations of Faulkner (Ref. 8) using $m_{\perp} = 0.180$, $\kappa = 10.75$, and $\gamma = 0.125$ or 0.117 for columns (A) and (B), respectively.
[d] Position of the zero-phonon recombination line of exciton bound to Te in GaP, 2.3102 eV at 2°K, minus ϵ_I(Te) = 89.8 meV.

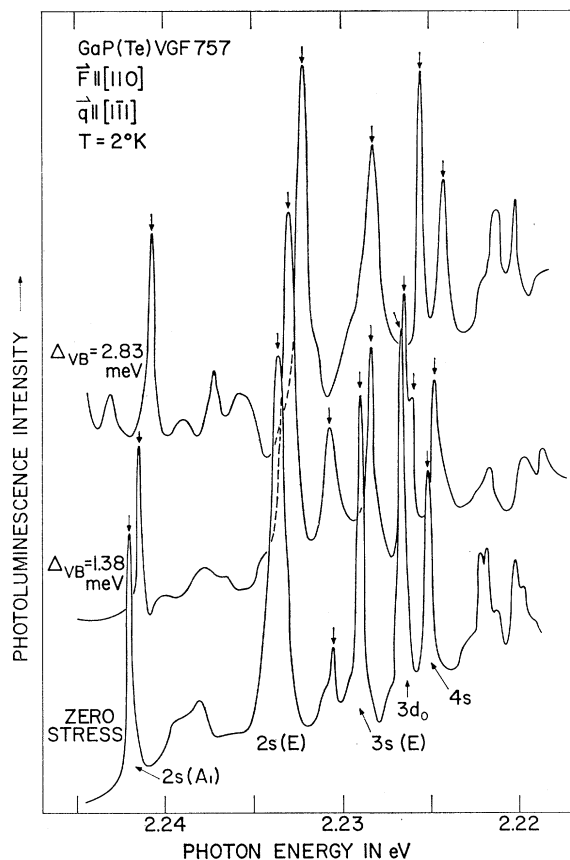

FIG. 3. The photoluminescence spectrum of Te-doped GaP in the region of the two-electron transitions. The lowest spectrum is with no externally applied stress on the sample. The upper spectra, displaced vertically for graphic clarity, are taken with external [110] uniaxial compression of the sample. Δ_{VB} denotes the valence-band splitting at those stresses. The lines are labeled by the proposed assignments of the final donor states involved in the transitions.

states, determined with parameters obtained from the infrared data, are also shown. The designations of the final states are made to conform to the notation used by Faulkner.[8] A valley-orbit splitting of the lower s-like states has been assumed.[7] The excited states observed in the two-electron spectra are believed to have even parity because their binding energies do not correspond to the odd-parity excited states observed in infrared excitation spectra.[1] It was suggested earlier by Faulkner[13] that these excited states are s-like because their binding energies could not be calculated in the EM approximation if their symmetry was assumed to be p-like.[4]

In spite of excellent EM calculations and precise values of physical parameters that enter therein, however, it is apparent in Table II that agreement between observed and calculated even-parity excited states is still marginal. To a great extent, this difficulty probably arises from the valley-orbit interaction in the even-parity states of multivalley donors.[7] However, no general treatment of the valley-orbit interaction exists that can explain quantitatively the differences between observed and EM binding energies of the s-like levels. We have measured the two-electron spectra with the sample under uniaxial compression in order to provide experimental verification of the s-like nature and valley-orbit splitting of the excited states observed in these spectra.

Figure 3 shows the two-electron spectrum with two magnitudes of uniaxial [110] stress applied. Figure 4 shows the positions of the peaks marked in Fig. 3 by downward pointing arrows as a function of applied stress. Additional stress data not shown in Fig. 3 are included in Fig. 4. The line positions in Fig. 4 are measured with respect to the low-energy stress-induced component of the zero-phonon recombination line of the exciton bound to Te in GaP. The line positions are plotted as a function of valence-band splitting due to the applied stress. The valence-band splitting is assumed to be linear in stress magnitude and equal to the splitting of the zero-phonon exciton recombination line and was measured in the same sample at 5°K. At 2°K,

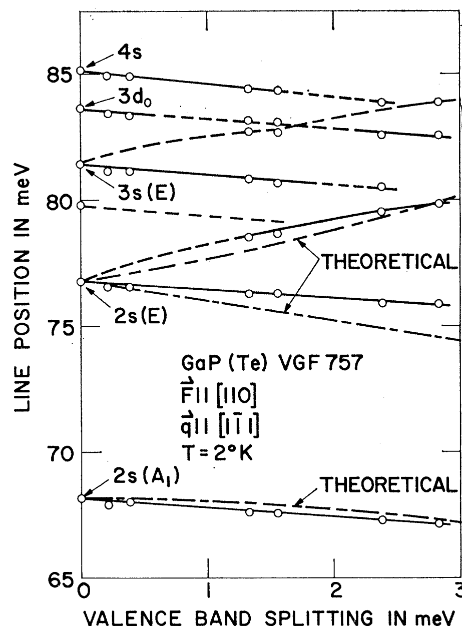

FIG. 4. Stress dependence of the two-electron transition lines observed in photoluminescence. The line positions are measured with respect to the low-energy component of the zero-phonon recombination line of excitons bound to neutral Te donors in GaP. This energy should correspond to the energy involved in the excitation $1s(A_1) \rightarrow ns$. The line positions are plotted against valence-band splitting: a parameter linear in stress magnitude with an estimated correspondence of $(\Delta_{VB}=1 \text{ meV}) = 0.27\times10^9$ dyn/cm². The polarization of the photoluminescence was not measured; however, the spectrograph would have been more sensitive to light polarized with the electric vector perpendicular to the stress direction versus parallel to the stress direction by a factor of about 1.5.

[13] Reference 39 in P. J. Dean and C. H. Henry, Phys. Rev. 176, 928 (1968).

except at the smallest stresses, the high-energy component of the exciton zero-phonon line was completely extinguished by thermal depopulation. Also shown in the figure are three theoretical curves representing the expected stress dependence of a valley-orbit split $2s$ level of the donor electron. The curves have been calculated assuming a valley-orbit splitting of 8.6 meV, a conduction-band shear deformation potential $\Xi_u = 6.9$ eV,[14] and the elastic compliance coefficients of GaP measured by Weil and Groves.[15] The calculation was done following the prescription of Price[16] and Wilson and Feher,[17] modified for the case of the three-valley conduction band.[18]

The effects of stress presented in Fig. 4 are consistent with the proposition that the excited states observed in two-electron transitions are s-like, with a valley-orbit splitting. As expected, the $2s(E)$ and $3s(E)$ levels split into two components and the $2s(A_1)$ level remains unsplit by the applied stress. No conclusions about the zero-stress degeneracies of the levels labeled $4s$, $3d_0$, and what may be the $3s(A_1)$ level at 79.8 meV can be drawn on the basis of the present data. It is observed that up to stresses where the high-energy component of $2s(E)$ would cross the $3s(A_1)$ level, the $2s(E)$ splitting is that expected theoretically (if it were the $2p_\pm$ level the splitting should be almost 50% larger). At larger stresses, the observed splitting is significantly smaller than expected. It is also noted that up to stresses where the high-energy components of $2s(E)$ and $3s(E)$ would cross the $3s(A_1)$ and $3d_0$ levels, respectively, the oscillator strengths of transitions to these levels are very small. From that point on, they increase markedly. Thus, the oscillator strengths of transitions to the high-energy components of $2s(E)$ and $3s(E)$ are apparently derived from a stress-induced mixing of these levels with other levels. This mixing probably accounts for the observed discrepancies between the experimental and theoretical curves in Fig. 4.

[14] I. Balslev, J. Phys. Soc. Japan Suppl. **21**, 101 (1966). The measured values of the elastic compliance coefficients from Ref. 15 have been used to correct the deformation potentials reported here.

[15] R. Weil and W. O. Groves, J. Appl. Phys. **39**, 4049 (1968).

[16] P. J. Price, Phys. Rev. **104**, 1223 (1956).

[17] D. K. Wilson and G. Feher, Phys. Rev. **124**, 1068 (1961).

[18] A. Onton and T. N. Morgan, this issue, Phys. Rev. B **1**, 2592 (1970).

V. CONCLUSIONS

Transitions of the type $1s(A_1) \rightarrow 2p_0$, $2p_\pm$ in Te donors in GaP have been observed. Together with similar data for Si and S donors in GaP[1] and the EM calculations of Faulkner,[8] these data yield an ionization energy of 89.8 ± 0.3 meV for Te donors in GaP. A 5% difference in the $2p_\pm - 2p_0$ splitting is observed for Te and Si donors, indicating a small donor-species dependence in the excited-state binding energies. All of the observed energy levels can be described by effective-mass calculations[8] if the conduction-band effective masses are taken as $m_\perp = (0.180 \pm 0.005) m_0$ and $m_{\parallel} = (1.5 \pm 0.2) m_0$. Donor ionization energies of S and Si in GaP consistent with these effective masses are 104.1 ± 0.3 and 82.1 ± 0.3 meV, respectively.

The effect of uniaxial [110] compression on the final states in two-electron transitions in the recombination spectrum of excitons bound to neutral Te donors has been investigated. The observed effects are consistent with the final states being s-like. Stress-induced mixing of some levels is evident in the data.

Note added in proof. Patrick and Dean[19] have recently obtained the value $\kappa = 10.75 \pm 0.1$ for the dielectric constant of GaP at 1.6°K. The dielectric constant enters into the results of this paper only in the effective masses calculated. The manuscript has been revised in accord with this new value for the dielectric constant:

$$\left(\frac{m_\perp}{m_0}\right) = \frac{\kappa^2 \epsilon_0}{Ry} = \frac{21.15 \times 10^{-3}}{13.60} \kappa^2 ,$$

$$\left(\frac{m_{\parallel}}{m_0}\right) = \frac{1}{\gamma} \left(\frac{m_\perp}{m_0}\right) .$$

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[19] L. Patrick and P. J. Dean, Phys. Rev. **188**, 1254 (1969).