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Potential-dependent electron and hole g values and quenched diamagnetism in GaP. I. Experimental results and properties of the donor states

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In this paper we present the results of an investigation of the radiative recombination of excitons bound to neutral S, Se, and Te donors in GaP in external magnetic fields of up to 16.5 T and, in one case, 18 T. The complete set of spectroscopic g values for the initial bound exciton and the final donor state and the different diamagnetic effects are evaluated for all three donors. This is the first report of diamagnetic effects in GaP. A diamagnetic shift and a splitting are observed, both anomalously small. A small tendency for an increase in the diamagnetic coefficients of the principal bound-exciton transition which leaves the donor in its ground state and a more dramatic increase for transitions to donor excited states with increasing quantum number are established. It is suggested that the principal two-electron lines all involve transitions to the $s(A_1)$ donor excited states. This new identification provides a more plausible position of the series limit E_{lim} of the donor than hitherto. The electronic g_e value of the donor turns out to be equal to 2.00, independent of the chemical nature of the donor. This value agrees with the value derived from ESR experiments. A recent supposition, that in general there might be a difference between luminescence and ESR g_e values is disproved. The isotropic hole g value is observed to decrease with increasing localization of the hole due to changes in the impurity central cell potential. These effects are given a detailed interpretation in the following paper.

I. INTRODUCTION

The luminescence spectra of excitons bound to neutral P-site donors in GaP provide an experimentally convenient means to check some very recent ideas on the dependence of the properties of localized states on the band structure of a semiconductor. Gallium phosphide has the degenerate Γ_8 valence band—typical of diamond or zinc-blende structure group IV or III-V semiconductors. Although the luminescence efficiency of excitons at neutral donors in GaP is low because of Auger recombinations,[1] a high proportion of the radiative recombinations contribute to the no-phonon lines for P-site donors. These lines are sharp in high-quality lightly doped crystals and are readily detected in the green near 2.31 eV, just below the band gap. The magnetic properties of these bound excitons were first reported by Thomas *et al.*[2,3] for the single donor S_P and at magnetic fields up to only 3 T. These authors discovered that the magnetic splittings of these bound excitons are much simpler than expected from the full degeneracy of the lowest set of equivalent conduction bands near the X zone-boundary points in this indirect-gap semiconductor. They suggested that interaction with the donor core potential splits the many-valley degeneracy by an amount large compared with the magnetic effects, producing a simple Kramers doublet low-lying ground state. The degeneracy of the bound-exciton state is simplified to that of the hole alone, since the states of both electrons are derived from a symmetric (singlet) superposition of valley states and the electron spins must be antiparallel from the exclusion principle. Later Morgan[4] noted that the properties of the Bloch part of the electron wave function near X ensures that this effect can only occur for donors on the electron-attractive (P) sublattice, although quasi-spin-orbit (spin-valley) splittings can reduce the degeneracy for electrons bound to Ga-site donors. These effects have been verified experimentally, also at low magnetic fields.[5,6]

The magnetic properties of the electrons in the P-site donors and of the bound-exciton complexes are both of great interest in the present work. In this paper we give the results of our experiments and discuss the magnetic properties of the donor states. For the first time diamagnetic effects are reported for GaP. In the following paper (hereafter referred to as II)[7] we show that it is possible to describe the most important magnetic properties of the bound exciton by a pseudoacceptor model with varying negative central-cell correction. This is analogous to a pseudodonor model which was recently successfully applied to the case of excitons bound to neutral acceptors.[8-11] To verify this model, we have to outline the theory of free holes and of effective-mass holes.

The linear splitting parameters of the S-donor bound exciton were not precisely determined in the early work[2,3] because of difficulties associated with accidental degeneracies of key magnetic subcomponents at low fields. These degeneracies are resolved at magnetic fields $\gtrsim 10$ T. We find that the electron g values are independent of the donor, S, Se or Te. They are identical

with previous estimates from electron spin resonance[12] as near as can be determined, as expected from our theoretical description and in contrast with recent speculations.[13]

The analysis of the diamagnetic properties of the donors is not as straightforward. The masses and the interaction energies of the different particles involved are comparable, which makes it difficult to derive diamagnetic shifts for an *individual* particle. This strongly contrasts with the situation for bound excitons in GaAs,[8,11,14] and GaSb,[9,10] where $m_e^* \ll m_h^*$ and the electron diamagnetism predominates.

However, we present some data on the differential diamagnetic shifts between the main no-phonon line and the "two-electron" satellites[15] of these donor bound excitons in GaP which show that the diamagnetism of the final state of the luminescence transition becomes predominant for the shallower donor states, causing an overall red shift contrasting with the blue shift of the principle transition. Problems associated with the earlier assignments of these satellites to specific donor excited states are briefly mentioned with reference to a recent, apparently more satisfactory interpretation to be reported elsewhere.[16]

Some of the results presented in this paper were briefly summarized at the 1975 International Luminescence Conference.[17]

II. EXPERIMENTAL

The crystals used in these experiments were of two types: small platelets freely nucleated from gallium solution grown by Curtiss of RCA Zürich, and small needles grown from the vapor with the wet hydrogen transport technique by Frosch of Bell Laboratories. The solution-grown platelets were nominally undoped but contained sufficient concentrations of S (and N) to exhibit intense sharp luminescence lines due to the recombination of excitons at these P-site substitutents. Some of the needles were also undoped and showed only very weak luminescence due to small residual concentrations of N and S, respectively, $<10^{14}$ cm^{-3} and $<10^{15}$ cm^{-3}. Other needles were specially back-doped with Se or Te to provide concentrations of these donors in the mid-10^{16}-cm^{-3} range. The platelets had ⟨111⟩-type large faces and were mounted with the magnetic field parallel to this axis. The needles had either ⟨111⟩ axes and ⟨112⟩ or ⟨110⟩ lateral surfaces as reported by Ellis *et al.*,[18] or ⟨100⟩ axes with ⟨100⟩ lateral surfaces. This latter morphology was not reported by Ellis *et al.*,[18] although it was noticed in the early growth work.[19] These needles were mounted both with H parallel to the needle axis (low fields) or H perpendicular to this axis and a selected lateral surface (high fields).

Two experimental arrangements were used for the magneto-optical measurements. In the first, a Bitter-type solenoid was arranged with 4880 Å exciting light from an Ar^+ laser directed along one horizontal radial-access (RA) port and incident on samples immersed in liquid He in a Dewar tail inserted down a second, vertical RA port while the luminescence was viewed along a third, horizontal RA port collinear with the first. The magnetic field was applied perpendicular to the plane of these RA ports and was restricted to 6.5 T in this arrangement. The second system comprised a simple axial access Bitter-type solenoid with a $1\frac{1}{4}$-in room-temperature bore arranged vertically. The tail of the sample immersion Dewar was inserted into the upper part of the bore. The lower part contained an output lens with a small access hole for exciting laser light and a system of external lenses and adjustable plane mirrors to enable the laser light to be brought to a sharp focus in the sample plane at the center of the magnet. An image of the luminescing crystal was focused with linear magnification of about 3 on the entrance slit of the 2-m $f/17$ Baird atomic spectrograph fitted with a 1200-lines/mm plane diffraction grating. The crystals were lightly fastened on a carousel in a circle of diameter ~1 cm mounted at the end of a sample wand with vertical axis arranged so that the samples could be brought in turn into the small region accessible to the laser beam by rotation of the wand from the top of the Dewar. It was important to be able to examine more than one sample for each liquid-He fill in this system since extreme precautions were necessary during liquid-He transfer to minimize the introduction of solid particulate contaminants which tended to settle out on the optical window at the bottom of the Dewar tail. Fine metal gauze filters at the input of the liquid-He transfer tube and at the top of the Dewar tail pipe significantly decreased the extent of this contamination. The magnetic field in this system was restricted to ~16 T with one optimum solenoid designed to match a 4-MW battery power supply and to 13 T with other solenoids driven by a mains powered 2.5-MW transformer-rectifier set. The spectra were all recorded photographically, thus obviating problems of the influence on the optical detector of the stray magnetic field and small residual mechanical vibrations from the Bitter magnet coolant system. Some confirmatory measurements on the two-electron transition diamagnetic shifts, which are small compared with a linewidth, were made

at magnetic fields up to 18 T at the Max-Planck-Institut Hochfeld-Magnetlabor, Grenoble, France. These spectra were recorded photoelectrically.

III. RESULTS

A striking feature of earlier experimental data on a variety of weakly bound excitons in GaP is the absence of any significant evidence of diamagnetic effects. This is true not only in the original work of Thomas *et al.*[2] at fields up to 3 T but also in subsequent work up to 5 T, for example the Ga site donor Sn,[5] the acceptor Cd,[20] the isoelectronic traps N (Ref. 21) and Bi.[22] It was clear that careful high-resolution measurements at magnetic fields well above 5 T would be needed to observe diamagnetic effects of bound excitons in GaP. This was a major motivation for this work, as well as the resolution of the accidental degeneracy which prevents the derivation of accurate linear magnetic parameters for the P-site donors as discussed in the introduction. It is interesting to note here that a generically similar system, the N donor exciton in β-SiC which has localization energy of the same order as GaP:Sn and GaP:Cd and about half that of GaP:S, also shows negligible diamagnetism at 3 T.[23] However, the linear g values are slightly different from GaP:S, and accidental degeneracy does not prevent the derivation of accurate g values even at 3 T. The derived electron g value is in fact consistent with the electron spin resonance result as near as can be determined, in contrast to the impression given by Cherlow *et al.*[12] in their comments on β-SiC.

A. Magnetic behavior of the principal bound-exciton transitions to the donor ground state

The most extended data obtained in the present work are for GaP:S, $\vec{H}\|\langle 111\rangle$ (Fig. 1). These experimental data were taken from several different platelets but are mutually consistent. There are two significant features compared with the low field data of Thomas *et al.*[2] First, the shifts of the four predominant magnetic subcomponents are distinctly nonlinear. This is most easily seen for the outer components 1 and 4, where there are no complications from the accidental degeneracy mentioned above. It should be noted here that the labeling 1, 2, 2a, 3, 3a, 4 differs from that used by Thomas *et al.*,[2] since the forbidden $\Delta m_j = 2$ transitions they labeled 1 and 6 were not observed in the refined crystals studied in this work and have been disregarded (Fig. 1 inset). The second significant feature is the appearance of the component 3a at fields $\gtrsim 13$ T. Most spectra were recorded with the He bath at 4.2 °K. Strong quenching of the intensity of luminescence components 2a, 4, and, particularly 3a is expected at 4.2 °K and high magnetic fields due to thermalization between the magnetic substates of the bound exciton. These substates are just those of the hole according to the model introduced in II and used for the construction in the inset of Fig. 1 which shows the linear splitting pattern expected for this bound exciton. It was observed that the relative intensity of components 1, 3, 3a and 4 could be increased relative to 2 by strong optical pumping at 4.2 °K bath, using 0.3 – 0.5 W output from the Ar^+ laser. Such an optically enhanced spectrum is shown in Fig. 2(a) and is compared in Fig. 2(b) with a spectrum recorded at lower optical pumping with the sample immersed in liquid H_2. The further increase in the intensity of components 3a and 4 relative to 3 at 20.6 °K is clearly apparent. Strictly the π-polarized components 2a and 3 (Fig. 3) are not expected to appear in the Faraday optical configuration used for these data. However, light scattering within the small irregular platelets and needles caused considerable depolarization of the light and strong violation of these polarization selection rules. This depolarization was clearly present in the luminescence of bound excitons at N isoelectronic traps[21] recorded simultaneously from these crystals.

The predicted intensity ratios of the σ components 1, 3a and 4, 2 are both 1:3.[24,25] Considering this, the depolarization and thermalization effects and the intensity ratios shown in Fig. 2, the assignments indicated in Fig. 1 inset are uniquely determined. We show in II, that the hole diamagnetism contains a term like $a + bm_j^2$ which causes a diamagnetic splitting between the $m_j = \pm\frac{1}{2}$ and $m_j = \pm\frac{3}{2}$ hole substates while the electron in the final state of the transition merely undergoes a diamagnetic shift. The differential diamagnetic shift to the blue between the exciton and donor states is clearly seen in Fig. 2 as a displacement of the center of gravity of the magnetic subcomponents above the energy of the zero-field line. However, we show in II that the diamagnetic *splitting* is of particular theoretical interest. It is also responsible for the failure to resolve components 2 and 2a even at 16 T if we recognize that 2 has a slightly larger linear magnetic shift rate to the red which is annulled over the accessible field range by a significantly larger diamagnetic shift rate to the blue, consistent with expectation from the form given above if b is positive [see Eq. (13) and Table III in II]. It is clear from Fig. 1 inset that the nonlinear shift rate of components 1, 4 is a measure of the relative diamagnetic shift rate between the $m_j = \pm\frac{1}{2}$ hole states and the donor

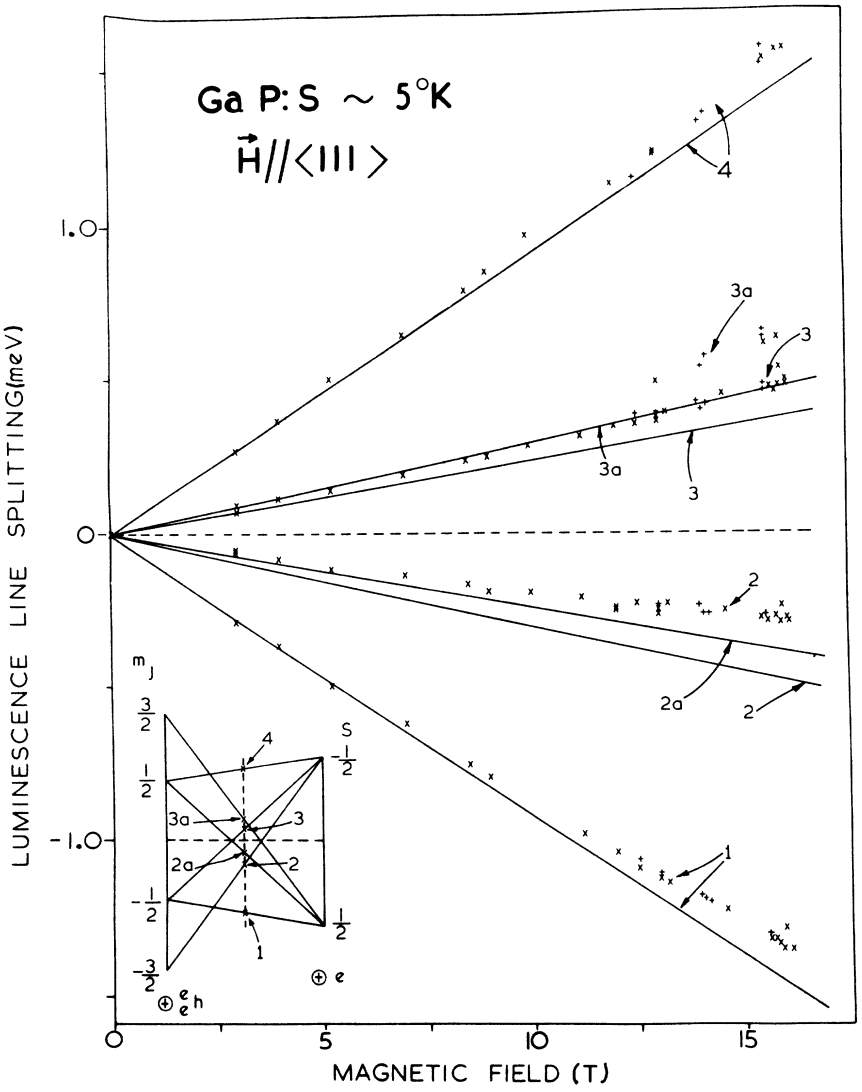

FIG. 1. Zeeman splitting of the principal no-phonon line due to the recombination of excitons bound to neutral S donors in GaP. The construction in the inset (Ref. 37) gives a key to the assignments of the observed magnetic subcomponents in terms of transitions between the indicated magnetic substates of the bound exciton, $m_j = \frac{3}{2}$ and the neutral donor, $m_j = s = \frac{1}{2}$. Diamagnetic effects are disregarded in this construction, but are significant in the data at magnetic fields above ~5T. The lines represent a fit using the linear g values in Table I.

state [Eq. (37) of II] and that this shift rate also applies to component three. These considerations fix the slopes of lines 1, 3, and 4 on Fig. 1, while $2a$ is simply obtained as the mirror image of 3 about the zero-field line (dashed). We see from this that the experimental points for $2a$ indeed lie almost coincident with those labeled 2, as just described, and remain unresolved from them. We label the observed experimental points 2 rather than $2a$ because of the large thermalization between the $m_j = +\frac{1}{2}$ and $m_j = -\frac{3}{2}$ hole substates. Thus, we obtain the linear magnetic splitting of the $\pm\frac{3}{2} \rightarrow \pm\frac{1}{2}$ transitions from the energy difference between observed components $3a$ and 2, and so estimate the position of lines $3a$ and 2 after subtraction of the diamagnetic shift. The linear and diamagnetic g values and energy shifts obtained from this procedure are shown in Tables I and II.

Our interpretation is qualitatively consistent with that of Yafet and Thomas,[3] but the ambiguities of their numerical analysis are removed and the diamagnetic effects are clearly resolved. The linear and diamagnetic effects for the separate bound-exciton and donor states are clearly shown in Fig. 3, including the phenomenological linear splitting parameters $g_{h,1/2}$ and $g_{h,3/2}$ of the Γ_8 hole state. The relationship between these parameters and the valence-band parameters is discussed in II. The different crystallographic orientations noted in Table I were selected purely from considerations of experimental convenience. The experimental convenience follows from the description in Sec. II of sample mounting on the carousel for the highest field experiments, since the available crystals of best optical quality were

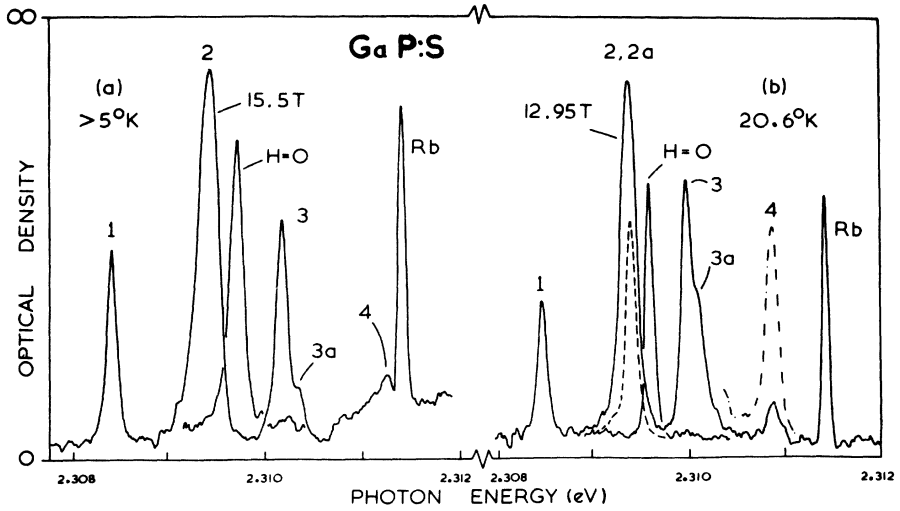

FIG. 2. Spectrum of magnetic subcomponents from the principal no-phonon line in the luminescence of excitons bound to neutral S donors in GaP. The spectra were recorded photographically (i) under high optical pumping with the crystal immersed in liquid He at 4.2 °K and (ii) at lower optical pumping and liquid H_2 at 20.6 °K. The dashed components in (ii) were recorded with four times longer or shorter exposures than the main full line spectrum. The labeling is consistent with the inset in Fig. 1. The single peak observed at zero field is shown located asymmetrically in each spectrum. The line marked Rb is from a calibration lamp.

S-doped platelets and Se- or Te-doped needles with (100) cross sections. This is not the optimum arrangement for analysis since the most difficult aspect is the precise estimate of the separation between components 3 and $3a$. The consequence of the changes in linear hole-splitting parameters in the sequence S → Te shown in Table I and interpreted in Table V of II is a small decrease in the separations of components 3 and $3a$, mostly because of a decrease in the term $3g_{h,3/2}$ for $\vec{H}\|\langle 111\rangle$, which directly reduces the larger shift rate of component $3a$. This trend is accentuated by changing the orientation from $\vec{H}\|\langle 111\rangle$, to $\vec{H}\|\langle 100\rangle$. The further reduction is mainly due to the effect on component 3, slightly increased in energy because of a reduction in $g_{h,1/2}$ from $2\tilde{\kappa}+\frac{13}{2}\tilde{q}$ to $2\kappa+\frac{1}{2}\tilde{q}$, where $\tilde{\kappa}$ is an isotropic and $\tilde{q}$ is an anisotropic hole g value as discussed in II, while $3g_{h,3/2}$ which governs the position of component $3a$, scarcely changes. However, the differential diamagnetism ensured that this critical splitting was still clearly seen in the original photographic data with $\vec{H}\|\langle 100\rangle$ for the back-doped needles, despite their slightly larger linewidth compared with the best inadvertently S-doped crystals. Most important, the small residual linear magnetic splitting of 2 and $2a$ allowed these components to be resolved just as well as 3 and $3a$ for $\vec{H}\|\langle 100\rangle$. A few measurements were made with other sample orientations, particularly needles which could be conveniently mounted with a lateral face perpendicular to $\langle 110\rangle$ to check the validity of the hole anisotropy parameters listed for Se and Te in Table V of II.

B. Zeeman effect of the donor states

Before we discuss the diamagnetic effects in the principal bound-exciton transition and in the two-electron satellites, we mention briefly the properties of the ground state of anisotropic donors in a magnetic field and report our measurements of the spin splitting of the donors.

TABLE I. Results of the linear Zeeman effect.

	λ_{air} (Å)	$h\nu$ (eV)	g_e	$g_{h,1/2}$	$g_{h,3/2}$	Direction of $\vec{H}$
S	5366.445	2.303 760	1.98 ± 0.01	1.165 ± 0.015	1.00 ± 0.015	⟨111⟩
Se	5370.193	2.308 148	1.99 ± 0.02	0.81 ± 0.03	1.03 ± 0.03	⟨100⟩
Te	5366.509	2.309 732	1.99 ± 0.02	0.84 ± 0.03	0.99 ± 0.03	⟨100⟩

TABLE II. Results of the diamagnetic effect.

	H (T)	Direction of $\vec{H}$	$\vec{E}_{dia}$ (meV)	Δ (meV)
S	15	⟨111⟩	0.14±0.01	0.063±0.15
Se	12.5	⟨100⟩	0.09±0.02	0.04 ±0.03
Te	12.5	⟨100⟩	0.11±0.02	0.05 ±0.03

The ground state of the donor has A_1 symmetry, which means that it is nondegenerate disregarding the Kramers degeneracy. In a magnetic field, this level splits into two components with spins parallel and antiparallel to the magnetic field, which should be separated by $g_e \mu_B H$, where g_e is the electronic g value, provided that this splitting is much smaller than the $A_1 - E$ valley-orbit splitting. Besides this splitting, the donor ground state experiences an angular dependent diamagnetic shift. This diamagnetic shift is proportional to the area of the orbit of the electron in a plane perpendicular to $\vec{H}$. In general these orbits are elliptical. The diamagnetic shift is

$$E_{dia} = e^2 a_0^2 H^2 / 4\mu c^2, \tag{1}$$

where $a_0 = a_B \epsilon_0 / \mu$ is the Bohr radius and μ is the reduced effective mass. For $\vec{H} \| \langle 100 \rangle$ we use

$$\mu = \sqrt{3}\, m_t (m_l m_t)^{1/2} / (2m_t^2 + m_l m_t)^{1/2}, \tag{2}$$

which gives $\mu(\langle 001 \rangle) = 0.378 m_\alpha$. With this mass value we get for the effective mass donor

$$E_{dia}(\langle 001 \rangle) = 2.8 \times 10^{-4} \text{ meV/T}^2 \tag{3}$$

Here we have used the mass values $m_t = 0.25 m_0$ and $m_l = 1.6 m_0$ which can be derived from Manchon and Dean's[26] Raman data together with Faulkner's[27] theory. There is some disagreement between these values and some very recent ones by Suzuki and Miura[28] and Leotin *et al.*[29] The reasons for our choice will be discussed in detail elsewhere.[16] The dielectric constant $\epsilon_0 = 11.02$ we use was determined by Vink *et al.*[30]

The g_e values of the final donor states were evaluated in a straightforward way from the experimental results presented in Sec. III A. Within experimental error, they are the same for all three donors: $g_e = 1.99$–2.00. Our results agree exactly with Title's[12] paramagnetic resonance measurements, which were also performed for all three donors S, Se, and Te. Thomas *et al.*[3] and Yafet *et al.*[4] derived a value of 1.89 ± 0.103 from some magnetoluminescence experiments on sulphur-doped material in fields up to 3.1 T. They observed four lines. The two outer lines were polarized perpendicular to the field, whereas the inner lines were not polarized. It is quite clear from the discussion in Sec. III A that their inner pair of lines consists of the two pairs of unresolved lines $3/3a$ and $4/4a$. Without knowing the exact position of at least one π line, one cannot derive a precise g_e value. Regarding this and given the fact that we were not only able to work at much higher fields but could also correct our results for the diamagnetic splitting the value of Thomas's can be seen to be a reasonable approximation. Cherlow *et al.*[13] recently reported the results of magnetoluminescence experiments on excitons bound to the neutral donor As in Si. They found a disagreement between the g_e value

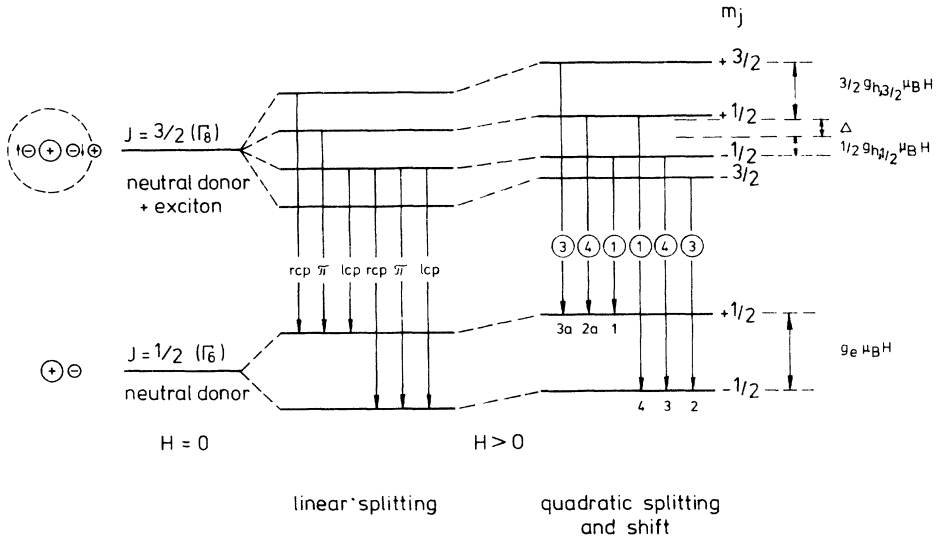

FIG. 3. Diagrammatic representations of the bound exciton, upper and neutral donor states, lower left and their linear and quadratic behaviors in a magnetic field, center and right. The circled numbers represent the relative intensities (Refs. 24 and 25) of the transitions at the right, labeled below in accordance with the inset of Fig. 1. The polarizations are shown in the center for the Faraday configuration, rcp means right circularly polarized, lcp left circularly polarized, π means $\vec{E} \| \vec{H}$. The origins of the linear g values of Table I and the diamagnetic splitting Δ of Table II are shown at the right.

they evaluated for the donor and the microwave value, which was larger. Their spectra although poorly resolved (e.g., Fig. 11) are clearly asymmetric, because of the diamagnetic splitting. If one corrects for these effects, one gets rough agreement with the microwave value. Cherlow *et al.*[13] suggested it might be generally true that photoluminescence experiments give smaller g_e values than microwave experiments. They supported this suggestion by a comparison of their own results, with the results of Thomas *et al.*[3] in GaP and others. We find[17] that there is no definite experimental evidence for this effect, as shown in the above discussion and we also cannot find any theoretical argument in favor of such a possibility.

C. Diamagnetic effects in the principal bound-exciton transition and in the "two-electron" satellites

The estimates of the mean and differential diamagnetic shifts of transitions from the $m_j = \pm\frac{3}{2}$ and $m_j \pm \frac{1}{2}$ hole substates shown in Table II contain the slight suggestion of a trend to higher values in the sequence S-Te. This is as expected from the general dependence of diamagnetism on the radii of the bound states [Eq. (38) of II)], in view of the quantum mechanical relationship for the size parameter of the localized wave function $a_0^2 = \hbar^2/2m^*E_B$ where E_B is a relevant binding energy of the electronic particles of mass m^*. However, this trend is poorly determined, of the same order as the experimental errors. Technical problems with the RRE Bitter magnets prevented an examination of the Se and Te donor excitons up to the highest magnetic fields shown for S in Fig. 1. This is a very unfortunate limitation in view of the abnormally small value of these diamagnetic shifts. This limitation was partly alleviated by a few measurements up to 18 T on the Se donor exciton at the Grenoble High Magnetic Field Facility. These results have been incorporated in Table II. The remarkably small order of these shifts is in itself a key result whose significance is discussed further in II. It is also shown that the differential diamagnetic shift due to the diamagnetic splitting between the hole substates is more readily interpretable than the mean shift because of uncertainties in the contribution to the latter of electrons in the bound exciton state.

The diamagnetic shifts have to be corrected for the small reduction factor from the diamagnetism of the transition final state, the ground state of the neutral donor. Again, because of Eq. (38) of II, and the arguments just presented, we expect a much larger correction to apply to the "two-electron" transitions[15] where the donor is left in a series of excited states of much smaller E_B and therefore much larger $\langle a^2 \rangle$. This expectation is verified by the results in Table III for the four strongest "two-electron" luminescence satellites shown in Fig. 4. These satellites contain at most ~1% of the intensity of the principal no-phonon line discussed above which itself has a quantum efficiency of only ~0.2%.[1] It has proved very difficult to obtain satisfactory spectra of these weak features using the optically less efficient RSRE bottom window Dewar high magnetic field system described in Sec. II. The results in Table III were obtained with the radial access system and are consequently limited to much lower fields where the shifts are considerably reduced. As near as can be determined, fragmentary data obtained at ~12 T (Fig. 5) are consistent with Table III using the expected quadratic field variation of the diamagnetic contributions to the line shifts. Somewhat clearer spectral shifts for the Se donor at 18 T is presented in Fig. 6. The principal feature of the data in Table III is the evidence of a significant trend towards an increasing diamagnetic *red shift* for transitions to the higher donor-excited states, with a relatively small diamagnetism for the satellite labeled $2s(A_1)$ in Fig. 4. The electron binding energy for the $2s(A_1)$ state is ~26 meV,[16] very comparable to exciton localization energies in Table I of II, whereas the lower-lying two-electron satellites all involve donor excited states with substantially smaller binding energies. In view of Eq. (37) of II, these results and the diamagnetic blue shift of the principal donor bound-exciton transition

TABLE III. Diamagnetic shifts of the $|-\frac{3}{2},-\frac{1}{2}\rangle$ two-electron transitions to the indicated donor excited states.

	H (T)	Direction of $\vec{H}$	Diamagnetic shifts (meV) (negative) $2s(A_1)$	$3s(A_1)$	$3d_0(A_1)$	$4s(A_1)$	$4d_0(A_1)$
S	6.5	⟨100⟩	~0.01	0.06	0.08	0.05	
Se	6.5	⟨110⟩	~0.02	0.05	0.08	0.06	
Te	6.5	⟨110⟩	~0.02	0.06 (broad)	0.09	0.06	0.14

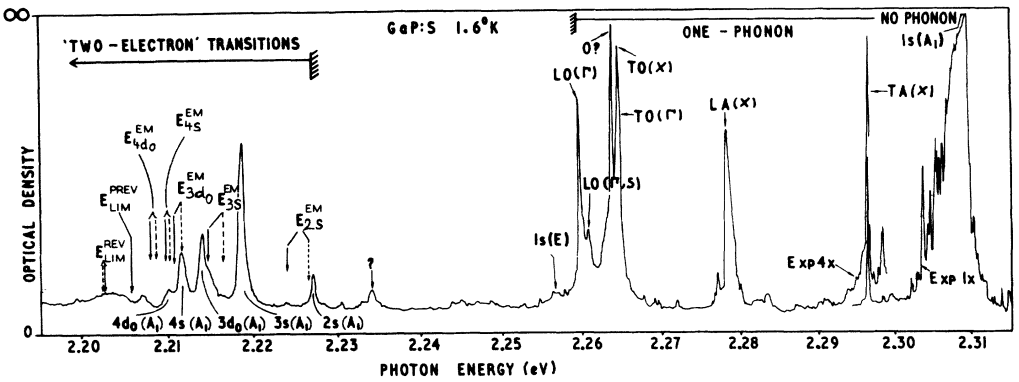

FIG. 4. Complete structure in the photoluminescence of excitons bound to neutral S donors in GaP, recorded photographically at 1.6 °K. The principal no-phonon transition at the right is heavily overexposed even at $\frac{1}{4}$ the exposure of the main spectrum. The weak fine structure on its low-energy tail arises from perturbation of the bound exciton by additional donors and acceptors (Ref. 38). The spectrum contains the phonon replicas of the principal transition to the $1s(A_1)$ donor ground state, involving phonons selected from momentum conservation, X, and low-wave-vector optical phonons $TO^{(\Gamma)}$, 0? $LO^{(\Gamma)}$ and LO (Γ, S) the latter introduced by the dielectric perturbation from the neutral donor. The "two-electron" transitions indicated below ~2.227 eV involve no-phonon recombinations which leave the donor in excited states, or in the conduction band below where $E_{\mathrm{LIM}}^{\mathrm{REV}}$ means revised series limit. The magnetic behavior of these "two-electron" transitions and the assignments of the related donor excited states is discussed in the text. The vertical arrows represent the effective mass theory estimates for the transitions to the indicated donor states for ellipsoidal conduction-band minima with $K=m_l/m_t=20$ (solid) and $K=30$ (dashed); E_{2s}^{EM} lies near the line labeled $3s$ (E) for $K=9$. The line labeled ? is not a persistent feature of the S-donor luminescence spectrum.

shown in Table II and discussed in II imply that the diamagnetism of the bound exciton state is larger than that of the electron in the ground state of these donors, while the reverse is true for transitions to the $2s(A_1)$ and particularly to the higher-lying donor excited states.

Unfortunately, the precision of the data in Table III does not justify a more quantitative analysis of this trend.

These Zeeman spectra also provide clear evidence that the linear splittings of the principal two-electron transitions are identical to those of the principal no-phonon line shown in Fig. 1. This confirms that at least those donor excited states responsible for these principal "two-electron" transitions are s-like[31] and shows that the relevant electron g value remains close to 2.00, as might be expected. S-like donor states should

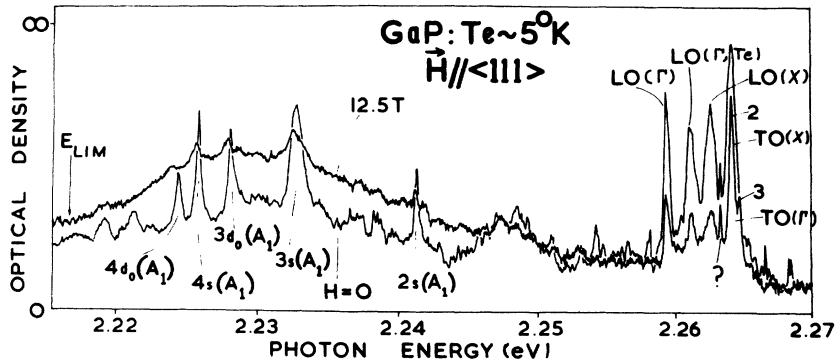

FIG. 5. A portion of the photoluminescence spectrum of excitons bound to neutral Te donors in GaP, recorded photographically at ~5 °K. To the right appear the optical phonon replicas of the principal line and the major "two-electron" transition satellites appear at the left. The former are labeled according to the optical phonon involved, and the latter according to the donor excited state as in Fig. 4. The optical phonon replicas have been aligned so that the shifts between the $H=0$ and $H=12.5$ T spectra at the left show directly the differential diamagnetism between the indicated donor excited states and the donor ground state.

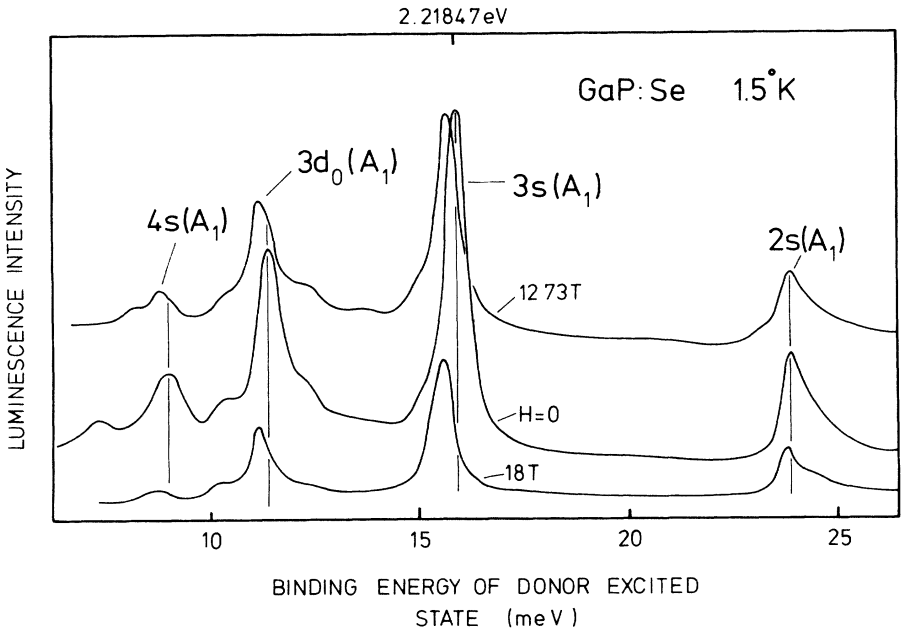

FIG. 6. Portion of the photoluminescence spectrum of excitons bound to neutral Se donors in GaP, recorded photoelectrically at ~1.5 K and containing only the two-electron transitions. The spectra have been aligned as in Fig. 5 to show the differential diamagnetic shifts between the donor ground state and the various indicated excited states at 18 T.

predominate if parity is a good quantum number, despite the lack of inversion symmetry in the GaP lattice. Parity conservation is consistent with the negligibly small magnitude of the cubic crystal field in the very extended states involved in these donor bound-exciton transitions, as is true even for the isoelectronic trap N.[21] No-phonon two-electron transitions to p-like donor states have been observed only for very shallow donors where the effects of the finite wave vector of the emitted photon are significant[32] and particularly in a large magnetic field where s and p states become mixed together.

The detailed interpretation of the energy positions of the "two-electron" transitions in GaP has proved difficult, initially because of misconceptions about the parity of the relevant donor excited states,[15,27,37] and more recently, because of the recognition of errors in some of the line assignments and in the key-electron effective-mass parameters m_t and $\gamma = m_t/m_l$ used in the first analysis[31] using the variational theory for s-like donor states associated with spheroidal conduction band minima.[27] The effective-mass theory estimates for the indicated s-like donor states in Fig. 4 have been made using the recent value of $m_t = 0.25m_0$, giving a Rydberg E_0 of 28.0 meV with $\epsilon_0 = 11$, and with $\gamma^{1/3} = 0.37$ defined from $K = 1/\gamma = 20$ derived from cyclotron resonance[29] (solid lines). The dashed lines were obtained for the larger value of $K = 30$ defined from the identification of the infrared Si donor photoexcitation peaks 4 and 1 of Onton[31] with transitions to states $2p\pm$ and $3p_0$.[33]

Each s-like donor state is expected to split into an (E) and (A_1) state by valley-orbit interaction according to the approximate model[2] for the conduction band minima in GaP in which there are three degenerate conduction band minima centered at the $\langle 100 \rangle$ zone boundary symmetry point X. The two electrons in the lowest bound-exciton state are both in the symmetric $1s(A_1)$ valley-orbit state, since the strong overlap with the donor core peculiarly characteristic of this state greatly enhances the binding energy as well as the no-phonon oscillator strength of the indirect bound-exciton transitions. No-phonon transitions to antisymmetric $s(E)$ donor excited states will be greatly weakened by the small overlap with the symmetric electron states in the exciton. This reduction in overlap must be very strong to explain the complete absence of a significant experimental feature near 2.257 eV in Fig. 4, the known position for transitions to the $1s(E)$ donor state according to electronic Raman scattering observed for the S_P donor in GaP.[26] These considerations indicate that the "two-electron" spectra belie their name in that the relevant transitions do not occur by a sequential process in which the indirect bound exciton recombines and then loses energy by inelastic scattering at the second electron, raising it to the $1s(E)$ excited state as allowed by the selection rules for electronic Raman scattering.[34]

We therefore suggest that the principal two-electron components all involve transitions to the

$s(A_1)$ donor excited states indicated at the bottom of Fig. 4. This contradicts the assignment of Onton and Taylor[35] who suggest in particular that the strong lines in the Te donor spectrum which correspond with those near 2.2185 and 2.2138 eV in Fig. 4 involve $s(E)$ states. However, their direct evidence for this assignment is not very conclusive. It involves the observation of a splitting of these transitions under uniaxial stress, unlike the equivalent of the S donor transition near 2.227 eV. Unfortunately, the experimental splittings are rather poorly substantiated, with no data for apparent splittings small compared with the zero-stress splittings when there is less scope for line misidentifications. The identification of the dominant "two-electron" line with transitions to the $2s(E)$ donor state also implies that the effective mass estimate for E_{2S}^{EM} cannot fall at higher luminescence transition energies, since experience with these spectra suggest that significant *negative* central-cell corrections are extremely unlikely. With $E_{2S}^{EM} \lesssim 16$ meV, $\gamma \lesssim 0.11$, $K \gtrsim 9.0$ according to the calculations of Faulkner,[27] in sharp disagreement with $K = 30$ given from the position of the $3p_0$ state with the *larger* binding energy of 18.7 meV. The likely relationship between K and binding energy is discussed elsewhere.[16] Unfortunately, it is not possible to differentiate between transitions to $s(A_1)$ and $s(E)$ donor states from our magnetic data since the E state does not split in a magnetic field.[5] Thus, the g factor is just that of the electron spin, like the A_1 state.

These new two-electron satellite identifications[16] provide a more plausible position of the true series limit E_{LIM}^{REV} (REV stands for revised) relative to the fine structure than that obtained previously from the value of $(E_D)_S$ tabulated by Vink *et al.*,[29] shown as E_{LIM}^{PREV} in Fig. 4. The change in E_{LIM} implies an increase in E_D of ~3.2 meV for all donors in GaP. The revised values for the P-site donors of particular concern in this paper are shown in Table I of II. The upper limit of the effective-mass ground state ionization energy of the S donor is 107–53.5 = 53.5 meV, since the $1s(A_1) - 1s(E)$ transition energy is 53.5 meV.[26] Thus, the effective K for this state is ~11.7, much smaller than the values used for the excited states in Fig. 4. This is as expected since the enhancement of m_t due to the camel's back structure of the absolute conduction band minima of GaP (Ref. 36) should be significantly reduced for a donor state of such relatively large binding energy. The implicit assumption that the $1s(E)$ state lies near E_{1S}^{EM} is consistent with the small donor dependence of the $1s(E)$ state deduced from the Raman spectra.[26]

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