region. Under maximum metal pressure firing conditions, a chalcogen vacancy mechanism may be operative. It is suggested that the mechanism for establishing chemical equilibrium as well as deviations from stoichiometry are dominated by the proposed neutral interstitials over most of the solidus region. It is further proposed that the only electrically active native defects are vacancies and that their concentrations may often be determined by interactions with chemical impurities rather than by the component partial pressures over the compound.

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Absorption and Luminescence of Excitons at Neutral Donors in Gallium Phosphide

P. J. DEAN
Bell Telephone Laboratories, Murray Hill, New Jersey

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Absorption and photoluminescence spectra of excitons weakly bound to sulphur, selenium, and tellurium donors in gallium phosphide have been studied at 25°K and below. Relatively weak satellite photoluminescence lines have been discovered. These photoluminescence satellites are phonon replicas, and some of the corresponding absorption satellites have been observed. Comparison with the intrinsic absorption-edge spectrum shows that some of these are the momentum-conserving (MC) phonons in the indirect transition. The more accurate estimates of these phonon energies provided from the bound exciton spectra are, (TA) 13.1±0.1 meV, (LA) 31.5±0.1 meV, (TO) 45.3±0.1 meV (sulphur spectrum). Replicas associated with the zone-center optical phonons, of energy 45.4±0.1 meV (TO) and 50.1±0.1 meV (LO), are also prominent. Luminescence spectra associated with the relatively heavy donors selenium and tellurium also contain prominent 23- and 47-meV phonon replicas which do not appear in absorption. These bands are apparently associated with "in-band resonance" local modes occurring at possible regions of low density of thelattice modes. The relative intensity of adjacent Mc (LA) replicas is increased when the local modes are prominent. Apart from this apparent interference with the local modes, the intensities of the optical and acoustical (MC) phonon replicas vary together between spectra involving different donors, as do the intensities of the no-phonon line and the zone-center replicas. The binding energy of the exciton to the donor does not vary as expected with the ionization energy of the donor or with the strength of the coupling to the momentum-conserving phonons. An absorption satellite 40.6±0.2 meV above the no-phonon lines for all three donors may also be a phonon replica, but is anomalously strong in the absorption spectra. Additional absorption satellites are apparently associated with excited states of the exciton–neutral-donor complex. The intensities of the satellites relative to the principal no-phonon line vary more than the relative transition energies between these three group-VI donors. The spectral positions of these excited states and the activation energy for thermal quenching of the luminescence intensity (29±1.5 meV) suggest the liberation of free electrons and holes rather than free excitons from these complexes.

I. INTRODUCTION

FINE structure was first reported in the edge absorption spectrum of gallium phosphide in 1961.[1] Later investigations have established a connection between the strength of a sharp absorption line near 2.31 eV and the concentration of neutral sulphur donors, and an additional absorption line ~1.5 meV to lower energies was observed in selenium-doped crystals.[2] Zeeman studies in photoluminescence have confirmed the view that these sharp lines involved excitons bound to neutral donors.[3] Comparison with the absorption spectra showed that the principal line involved a no-phonon transition, in contrast to an earlier conclusion.[2]

Phonon replicas of the sulphur-bound exciton luminescence line (the *C* line) have not been reported. Weak satellite structure was observed in the absorption spectra of sulphur-doped crystals,[2] but incorrectly interpreted due to the misidentification of the no-phonon line and to the contemporary lack of information concerning the relevant phonon energies in gallium phosphide.

The present paper is devoted to a detailed examination of the principal absorption-luminescence systems due to excitons bound at neutral sulphur, selenium, and

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[1] E. F. Gross, G. A. Kalyuzhauya, and D. S. Nedzvetsky, Fiz. Tverd. Tela **3**, 3543 (1961) [English transl.: Soviet Phys.—Solid State **3**, 2573 (1961)].

[2] M. Gershenzon, D. G. Thomas, and R. E. Dietz, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* 1961 (The Institute of Physics and The Physical Society, London, 1962), p. 752.

[3] D. G. Thomas, J. Gershenzon, and J. J. Hopfield, Phys. Rev. **131**, 2397 (1963).

tellurium donor centers in gallium phosphide. Weak luminescence satellites have been discovered, which are phonon replicas associated both with momentum-conserving (MC) phonons required by the indirect electronic interband transition[4] and with optical phonons of negligible momentum.[5] Replicas involving some of these phonons can be identified in the absorption spectra, which also exhibit structure apparently connected with excited electronic states of the exciton complex. A relatively weak luminescence replica of energy 48.9±0.2 meV is tentatively identified with the longitudinal optical phonon at the $\langle 100\rangle$-type zone boundaries (X symmetry point, phonon LO^X). Replicas of energy 23.0±0.2 meV and 46.8±0.1 meV, which are prominent in the luminescence spectra of excitons bound to neutral selenium and tellurium donors but not in the corresponding absorption spectra, are attributed to "inband resonance" local modes introduced by these heavy substitutional impurities. According to the theory of local modes introduced by heavy substituent impurities,[6] this classification of the sharp 46.8-meV replica predicts a minimum in the density of lattice states near this energy. Consistent with the assignment suggested for the X phonons, this prediction implies that the LO and TO dispersion curves of gallium phosphide converge but do not cross as the wave vector increases within the reduced zone. This prediction is contrary to the trend noted for zincblende-type semiconductors between the behavior of these optical phonons and the magnitude of the effective ionic charge.[7] The relationship between the intensity of the no-phonon absorption line, the binding energy, E_{Bx}, of the exciton at the netural donor and the character of the phonon interactions is discussed qualitatively and comparisons are made between these properties of exciton-neutral donor complexes in gallium phosphide and in other indirect-type semiconductors. Measurements of the thermal quenching of the luminescence indicate that these bound exciton complexes in gallium phosphide dissociate by the emission of free-electron–hole pairs rather than free excitons.

II. EXPERIMENTAL

A. Crystal Growth

1. *Absorption Spectra*

It is relatively easy to grow crystals of gallium phosphide $\lesssim 1$ mm thick from floating zone-refined material, from gallium solution or by vapor transport which are sufficiently doped with sulphur to show the C-bound-exciton absorption line. Zone-refined grown crystals were used in the original identification of the C line with the neutral sulphor donor.[2] A harder task is the production of crystals which are adequately doped yet sufficiently strain free to show the fine structure in the relatively weak satellite absorption lines at energies above the C line, since doping with donors apparently has an adverse effect on the crystal growth mechanism and on the degree of perfection of the resulting crystals. At neutral donor concentrations $\gtrsim 10^{18}$ cm^{-3}, the crystals generally contain internal strains sufficient to appreciably broaden the C line and thereby obscure the details of the satellite structure.

The best absorption spectra were generally obtained by using needles of gallium phosphide doped in the concentration range $10^{17} \rightarrow 10^{18}$ cm^{-3} prepared by the hydrogen transport process which provided a path length of ~ 5 mm for the absorption measurements. Selenium or tellurium was added as vapor from the elemental sources carried by dry hydrogen into the main wet hydrogen stream at a point between the gallium phosphide polycrystalline source material and the growth zone for needles.[8] Significant strain broadening of the principal exciton absorption line was still generally obtained with $\gtrsim 10^{17}$ cm^{-3} neutral donors, however.

An exceptionally well-resolved absorption system associated with sulphur donors was obtained using an unintentionally doped 6-mm by 4-mm by 1-mm plate grown epitaxially on a gallium phosphide seed by the halide process.[9]

Many heavily doped needles exhibited light scattering sufficient to prevent high-resolution absorption measurements. These crystals were customarily quenched rapidly in air from their growth temperature of ~1100°C. One needle was subsequently annealed from 800°C in air over several hours. Little reduction in the half-height bandwidth of the C-absorption line was produced, but the general absorption level near the intrinsic edge increased by more than an order of magnitude.

2. *Luminescence Spectra*

Crystals containing a high concentration ratio of neutral donors to isoelectronic nitrogen centers are necessary for a detailed study of the C phonon replicas, since the interaction of the C line with phonons is much weaker than that of the A line.[3] Only the transverse acoustical C replica stands above the high-energy threshold of the persistent type-I_A[10] donor-acceptor pair spectrum, so an additional requirement is that the concentration of the I_A acceptor center should also be low.

Polycrystalline flakes of gallium phosphide prepared by the phosphine open-tube gas-flow process at 800°C[11] were mainly used for the luminescence studies. The gallium and furnace tube components were baked out

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[4] P. J. Dean and D. G. Thomas, Phys. Rev. **150**, 690 (1966).

[5] M. V. Hobden and J. P. Russell, Phys. Letters **13**, 39 (1964).

[6] P. G. Dawber and R. J. Elliott, Proc. Phys. Soc. (London) **81**, 453 (1963).

[7] R. W. Keyes, J. Chem. Phys. **37**, 72 (1962). See also S. S. Mitra, Phys. Rev. **132**, 986 (1963).

[8] C. J. Frosch, in *Proceedings of the International Conference on Crystal Growth, Boston, 1966* (Pergamon Press, Inc., New York, 1967), p. 305.

[9] W. G. Oldham, J. Appl. Phys. **36**, 2887 (1965).

[10] D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. **133**, A269 (1964).

[11] C. J. Frosch and G. S. Rao (private communication).

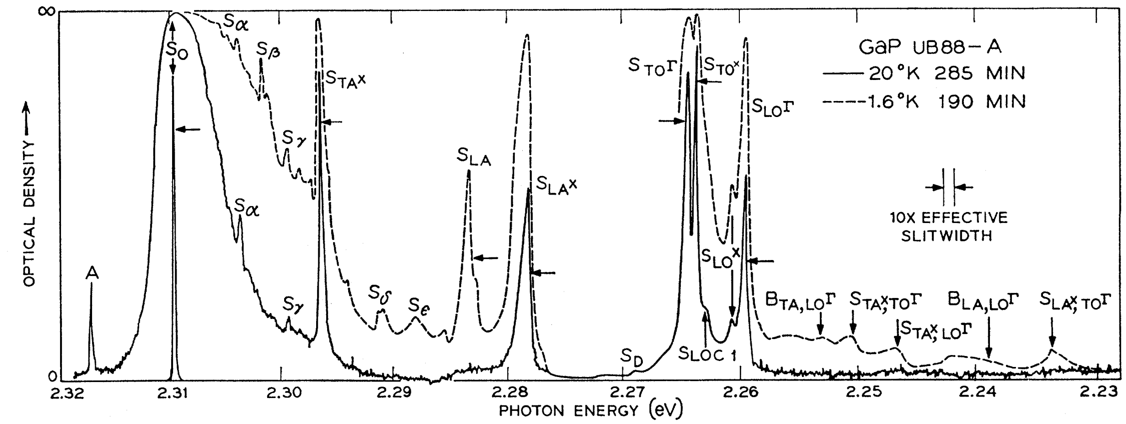

FIG. 1. Luminescence spectra of excitons bound to neutral sulphur donors in gallium phosphide obtained from photographic plates using a densitomer. Crystal UB88A exhibited minimal strain broadening of the no-phonon line S_0. The exposure for S_0 is ~1/1100 of that used for the lower-energy dashed components. The dashed spectrum was measured at 1.6°K, where luminescence due to excitons bound to isoelectronic nitrogen impurities (A,B system) was significant. Portions of this spectrum near 2.27 eV and above 2.31 eV, where the luminescence was predominantly due to the A, B transitions, have been deleted for clarity.

at 1100°C in a stream of hydrogen before the synthesis to reduce the concentrations of both the nitrogen and the I_A pair spectrum acceptor.[12] The concentration of these acceptors is apparently reduced either by using a dry hydrogen-phosphine gas flow mixture and a boron nitride boat and furnace liner to exclude contamination from quartz components, or by using an all-quartz system with a wet hydrogen-phosphine mixture. Synthesis at 1100°C produced larger single crystals, but gave weak C line luminescence unless, as in earlier experiments,[11] the phosphine was generated by reacting water and aluminum phosphide, which is appreciably contaminated with sulphur.

Selenium-doped crystals were prepared by adding 0.0001% of selenium or cadmium selenide to the gallium and using the 800°C synthesis described above. Most of the cadmium evaporates away during the 1100°C bakeout, but the luminescence spectra indicated that sulphur was always present as well as selenium, possibly because sulphur is a contaminant of selenium.

Tellurium-doped crystals were prepared by a similar method at 800°C using an all-alumina furnace tube and boat. Very low concentrations of nitrogen were generally obtained. The maximum intensity of the tellurium bound exciton luminescence system relative to the type I_B donor-acceptor pair spectrum associated with the irreducible background concentration of acceptor centers was obtained with crystals grown from gallium containing 0.001% of tellurium.

B. Apparatus

Optical measurements were made using a Spex $F/6.8$ Czerny-Turner grating monochromator with an EMI 9558 photomultiplier detector. The crystals were mounted in a variable temperature cryostat in which the sample temperature was controllable between ~23 and ~150°K by a stream of cold hydrogen gas generated in a liquid-hydrogen reservoir.[13]

Some luminescence measurements were made with the crystals immersed in liquid hydrogen or liquid helium using a 2-m $f/17$ Bausch and Lomb grating monochromator with a photographic plate detector. The luminescence was excited by two HBO 200 high-pressure mercury arcs, each of which was equipped with two 3.5 mm Corning 7.95 optical filters to reduce the intensity of stray mercury light at ~5400 Å to a negligible level.

III. RESULTS AND DISCUSSION

A. Luminescence Spectra

1. *General*

In order to enhance the C-line luminescence relative to the residual donor-acceptor pair luminescence it is useful to work at very low temperatures to reduce the thermal quenching of the bound exciton transition. For many of the crystals studied, it proved better to make luminescence measurements at 20°K rather than at 4.2°K, however, since the residual A-line intensity was sometimes inconveniently large at the lower temperature. High excitation intensities are also useful since the oscillator strength of the C line is much larger than for even the highest-energy donor-acceptor pair line and the pair transitions therefore show saturation effects relative to the bound exciton lines at high excitation levels.[10]

2. *Energies of Phonon Replicas*

Figure 1 shows the C line and its associated phonon replicas observed in luminescence at 1.6 and 20°K. The spectral lines are labeled according to the nature of the

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[12] D. G. Thomas and R. T. Lynch, J. Phys. Chem. Solids **28**, 433 (1967).

[13] K. Maeda, J. Phys. Chem. Solids **26**, 595 (1965).

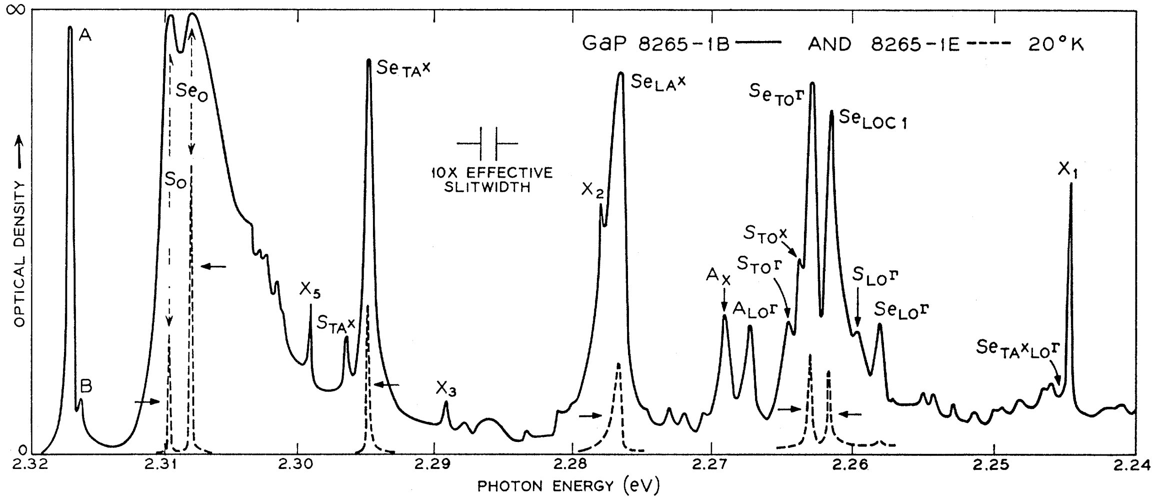

FIG. 2. Luminescence spectra of excitons bound to neutral sulphur and selenium donors in gallium phosphide. The spectra were obtained from photographic plates using a densitometer. The greater relative strength of the phonon replicas associated with selenium phonons is clearly shown in the full-line spectrum from crystal 8265-1B, where the exposure time was 420 min. The sharp lines denoted by X are members of a series associated with the presence of nitrogen, and lines A, B are due to no-phonon recombinations of excitons bound to isoelectronic nitrogen impurities. The numerous unlabeled weak but sharp lines below X_3 are due to electron-hole recombinations at donor-acceptor pairs, mainly involving selenium donors. The dashed components were obtained from the relatively strain-free crystal 8265-1E, using exposures of $\frac{1}{2}$ min for S_0 and Se_0 and 10 min for the phonon replicas.

donor center, and the subscript denotes the type of phonon involved in the transition. The complex fine structure on the low-energy tail of the no-phonon line S_0 (e.g., S_α and S_γ, respectively, 5.8 and 10.3 meV below S_0) is often observed in the luminescence of shallow bound excitons in gallium phosphide. This structure generally becomes more complex at very low temperatures, as is apparent in Fig. 1, where it is particularly remarkable that at 20°K there is no trace of the relatively strong line S_β (8.1 meV below S_0) observed at 1.6°K. The relatively broad weak lines S_δ and S_ϵ, respectively, 18.5 and 21.6 meV below S_0, may also be a part of this system since these energies do not suggest their identification with phonon replicas. The origin of this structure is unclear at present, and it will be disregarded in this paper (see Sec. III A 5, however).

The low-energy tail of S_0 which underlies this fine structure stretches to a relatively well-defined cutoff ~18 meV below S_0. A low-energy tail of similar extent is also observed for the no-phonon luminescence lines of excitons bound to neutral selenium (Se_0 in Fig. 2) and tellurium (Te_0 in Fig. 3) donors. There is a cutoff in the low-energy tail of the lowest-energy phonon replica of the A line also 18 meV below the A line.[14] These results suggest that this tail is connected with TA phonon-assisted transitions. The shape of the tail in the spectra of Figs. 1–3 suggests that the coupling is much greater for low-energy, and therefore long-wavelength, acoustical phonons. This is expected since the donor and exciton states have wave functions which are very diffuse compared with the unit cell of gallium phosphide. Similar low-energy tails have recently been observed in the Raman scattering spectra of neutral acceptor centers in GaP.[15]

The horizontal arrows in Figs. 1–3 denote the half-intensity points of the luminescence bands according to an independent calibration of the photographic plates.

The 20°K luminescence spectrum shown in Fig. 2 is dominated by the decay of excitons at neutral selenium donors, although the $C(S_0)$ and A lines are also present. It is fortunate that the phonon replicas are stronger relative to the no-phonon line in the selenium spectrum than in the sulphur spectrum, so that the sulphur replicas are negligible in Fig. 2.

Intercomparison of the *acoustical* phonon energies listed in columns (2)–(5) of Table I leads to the unambiguous assignments given in column (1). The intensity distribution amongst the optical replicas is sensitively dependent upon the nature of the donor and the energy comparison is therefore less straightforward. In particular the TO^X replica identified in the sulphur spectrum is not seen from selenium, whereas the LOC 1 replica, which is very weak for sulphur, is strong for selenium. Reasons are given in Sec. III C for the identification of the 45.9-meV sulphur replica with the TO^X phonon, whose energy can only be estimated relatively inaccurately in the intrinsic absorption spectrum,[4] (see the footnote in Sec. IV, however), and also for the association of the 46.8-meV replica with an "inband resonance" local mode produced by the substitutional impurity atom.

The weak 48.9-meV phonon replica, observed clearly only in the sulphur spectra since the selenium and

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[14] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).

[15] C. H. Henry, J. J. Hopfield, and L. C. Luther, Phys. Rev. Letters **17**, 1178 (1966).

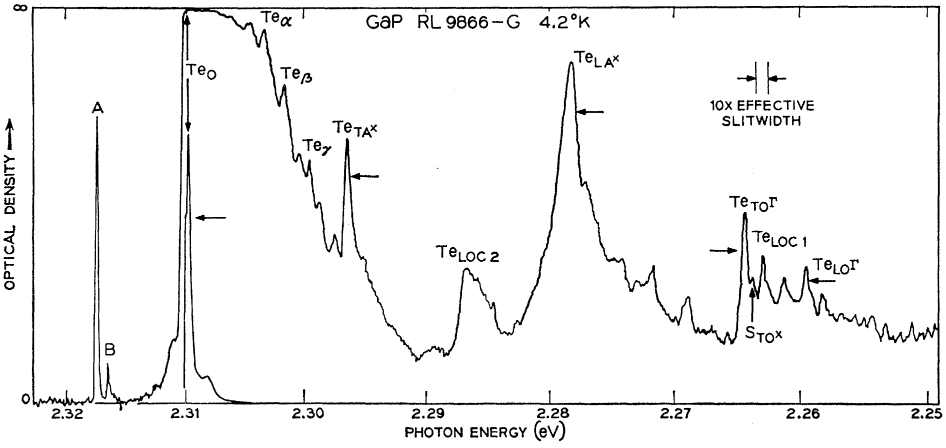

FIG. 3. Luminescence spectrum mainly of excitons bound to neutral tellurium donors in gallium phosphide obtained from a photographic plate using a densitometer. The exposure showing Te_0 resolved was 1/165 of that in the main spectrum showing the phonon satellites. The relatively weak unidentified bands below 2.29 eV are due to electron-hole recombinations at donor-acceptor pairs, mainly involving tellurium donors. Lines A, B are due to no-phonon recombinations of excitons bound to isoelectronic nitrogen impurities.

tellurium replicas could not be examined in adequate detail, is attributed to the LO^X phonon. The LO^X intrinsic absorption component is much too weak to be detected.[4] The energy of the LO^X phonon was previously[4] assumed to be ~44 meV, as suggested from interpretations of the second-order Raman spectrum,[5,16] but this is not compelling evidence. The higher value is now preferred for several reasons

(a) A 48.4-meV phonon is prominent in the luminescence spectrum of the A-bound exciton,[14] and a plausible assignment according to the symmetry properties of this center is LO^L. It is unlikely that the LO phonon branch would exhibit appreciable anisotropy across the surface of the reduced zone.

(b) The intensity ratio of the LA^X and LO^X replicas in Fig. 1 is ~25:1. This value is consistent with the enhanced coupling to the LA phonon consequent upon the favorable energy denominator in the transition matrix element for indirect transitions via the Γ_1 intermediate state, which are allowed only for this phonon.[4]

(c) If LO^X lies above TO^X as suggested in Table I, and the anisotropy in the TO and LO branches is small within the reduced zone, then for plausible dispersion curves along the Γ-$X(\langle 100\rangle)$ and Γ-$L(\langle 111\rangle)$ crystal axes these branches will not intersect. Thus there will be a narrow region, probably between ~46 and ~48 meV, where the density of states of the intrinsic lattice vibrations is zero. It is just such a feature which is required for the production in this energy interval of an intense narrow local mode by a sufficiently heavy substitutional impurity atom like selenium, as described in Sec. III C.

It is interesting to note that this proposal suggests that the behavior of the LO and TO lattice vibrational branches in gallium phosphide is more like that found experimentally in silicon carbide, where these branches do not cross,[17] rather than in gallium arsenide, where they cross at points well inside the zone both for the $\langle 100\rangle$ and $\langle 111\rangle$ symmetry axes.[18] This similarity and difference is reasonable, since for the X phonons, the LO and LA branches must become degenerate as the zinc blende lattice transforms to the diamond lattice. This will make it likely that LO^X will lie below TO^X for a zinc blende crystal with atoms of nearly equal mass ($M_{\mathrm{Ga}}/M_{\mathrm{As}} \sim 0.93$), whereas the LO^X-LA^X splitting may be large if this mass ratio is significantly different from unity ($M_{\mathrm{Ga}}/M_{\mathrm{P}} \sim 2.3 \sim M_{\mathrm{Si}}/M_{\mathrm{c}}$), and LO may be above TO throughout the zone. On the other hand, a relationship has been established between the behavior of the "density-of-states" optical-phonon energies of zinc-blende-type semiconductors, determined from the two-phonon infrared absorption bands, and the magnitudes of the effective ionic charge determined from reststrahlen spectra.[7] This relationship suggests that the LO and TO branches cross within the reduced zone for gallium phosphide, but not for silicon carbide. The present assignment of these optical replicas must therefore be regarded as tentative in the absence of more definitive experimental data.

The association of the weak components below 2.25 eV in Figs. 1 and 2 with multiphonon assisted transitions is also relatively tentative, although the combinations given in Table I are likely for two-phonon processes.

3. *Momentum Conservation and Phonon Replicas for Indirect Bound Exciton States*

A striking difference between the phonon replicas of the A line[14] and those shown in Figs. 1–3 is the relative sharpness of the acoustical phonon replicas of

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[16] J. P. Russell, J. Phys. (Paris) **26**, 629 (1965).

[17] D. R. Hamilton, W. J. Choyke, and L. Patrick, Phys. Rev. **131**, 127 (1963).

[18] J. L. T. Waugh and G. Dolling, Phys. Rev. **132**, 2410 (1963).

TABLE I. Comparison of phonon energies derived from the luminescence spectra of excitons bound to neutral shallow donors, from the intrinsic absorption edge spectrum and from first-order Raman scattering in gallium phosphide. All energies are in meV. TA, denotes transverse acoustical; LA, longitudinal acoustical; TO, transverse optical; LO, longitudinal optical.

Phonon[a]	Sulphur donor exciton replica	Selenium donor exciton replica	Tellurium donor exciton replica	Intrinsic absorption edge spectrum[b]	First-order Raman spectrum[c]
TA^X	13.0±0.1 (0.18)[b]	13.1±0.1 (0.21)	13.1±0.1 (0.51)	12.8±0.5	
LOC 2			23.0±0.2		
LA^X	31.5±0.1 (0.98)	31.5±0.1 (0.78)	31.5±0.1 (1.3)	31.3±0.5	
D	40.5±0.2				
TO^X	45.9±0.1 (0.15)			46.5±1.0	
LOC 1	46.7±0.2	46.8±0.1 (0.29)	46.8±0.2		
TO^Γ	45.2±0.1 (0.29)	45.4±0.1 (0.24)	45.4±0.1 (0.56)		45.43±0.1
LO^X?	48.9±0.2				
LO^Γ	50.1±0.1 (0.34)	50.1±0.2	50.1±0.1 (0.51)		50.05±0.1
TA^X, TO^Γ	59.0±0.5				
TA^X, LO^Γ	63.0±0.5	62.5±0.5		63.1±0.2[e]	
LA^X, LO^Γ	77.0±0.5			76.9±0.2[e]	

All energies are in meV
* Energies calculated by combining data in Columns (5) and (6).
TA–denotes transverse acoustical
LA–longitudinal acoustical
TO–transverse optical
LO–longitudinal optical

[a] Superscripts X and Γ, respectively, denote phonons from the ⟨100⟩-type boundaries or from the center of the reduced zone in the usual dispersion diagram for lattice vibrations. The association of lattice phonons from X with the MC phonons necessary for indirect interband electronic transitions is discussed in Ref. 4.
[b] Reference 4.
[c] Reference 5.
[d] The bracketed numbers denote the half-height bandwidths of the phonon replicas (in meV). Note that the assignment of the TO^X phonon is revised in a *note added in proof* (Sec. IV).
[e] Energies calculated by combining data in columns (5) and (6).

the S_0, Se_0, and Te_0 lines. The half-height bandwidths of the replicas in the sulphur, selenium, and tellurium bound exciton systems are indicated by the bracketed numbers in column (1) of Table I, measured for crystals in which the no-phonon line was relatively unaffected by internal strain (half-height bandwidth only ~0.09 meV for S_0 in Fig. 1 and for Se_0 in Fig. 2, spectral resolution 0.09 meV). The TA and LA phonon replicas of the A line have half-height bandwidths of ~5 and ~2.5 meV, and, in contrast to Figs. 1–3, there is a strong continuum underlying the peaks in the phonon spectrum. The energy distribution of the density of acoustical phonons throughout the reduced zone is apparently of more consequence in phonon coupling at the nitrogen impurity than the requirement of momentum conservation for the indirect transition, whereas the reverse is true for the replicas associated with the exciton-neutral donor complexes.

The luminescence spectra of bound exciton complexes in germanium,[19] silicon,[20] diamond,[21] and cubic[22] and hexagonal[17] silicon carbide suggest that interaction with MC phonons is generally predominant for complexes involving shallow neutral donors and acceptors in semiconductors with indirect energy gaps. A criterion for the importance of the MC replicas may be the ratio of the binding energy, E_{Bx}, of the exciton to the center and the internal binding energy, E_x, of the exciton. Appreciable deviations from the MC phonons are observed in the luminescence of excitons bound to ionized donors in silicon carbide, where $E_{Bx}/E_x \gtrsim 3:1$.[17] The MC replicas are still prominent in the luminescence of excitons bound to neutral indium acceptors in silicon where, as for donors in gallium phosphide (Sec. III B 2), $E_{Bx}/E_x \sim 2:1$. The predominance of the no-phonon lines in Figs. 1 and 2 is qualitatively consistent with a ratio of $E_{Bx}/E_x > 1$.

The phonon cooperation of the A-bound exciton transition, where $E_{Bx}/E_x \sim 1$,[4] does not conform to these general predictions.[3] It is now known that this transition involves an exciton complex of a different type, namely an exciton bound to an isoelectronic impurity center.[14] Comparisons of properties of the A and C systems will be complicated by this difference. At present the binding of the exciton to the isoelectronic center, which provides a large oscillator strength for this transition at the indirect energy gap,[23] is not understood in detail, however.

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[19] C. Benoit à la Guillaume, and O. Parodi, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press, Inc., New York, 1960), p. 426

[20] J. R. Haynes, Phys. Rev. Letters 4, 361 (1960).

[21] P. J. Dean, E. C. Lightowlers, and D. R. Wight, Phys. Rev. **140**, A352 (1965).

[22] W. J. Choyke, D. R. Hamilton, and L. Patrick, Phys. Rev. **133**, A1163 (1964).

[23] J. D. Cuthbert and D. G. Thomas, Phys. Rev. **153**, 763 (1967).

TABLE II. Comparison of the integrated intensities of phonon replicas, measured relative to the no-phonon lines, obtained from luminescence and absorption spectra of excitons bound to neutral sulphur and selenium donors in gallium phosphide.[a]

Phonon	Sulphur donor Luminescence	Sulphur donor Absorption	Tellurium donor Luminescence	Tellurium donor Absorption	Selenium donor Luminescence	Selenium donor Absorption
TA^X	0.87±0.05	1.1±0.2	2.1 ±0.3	2.0±0.5	5.0 ±0.2	5.3±0.5
LOC 2			5.1 ±0.4			
LA^X	1.5 ±0.1	2.0±0.5	13±2	3.0±0.5	8.4 ±0.3	8.5±0.5
TO^X	1.26±0.1	~1				
LOC 1			0.30±0.05		3.2 ±0.3	
TO^Γ	1.64±0.1	1.5±0.3	1.5 ±0.2		4.0 ±0.3	
LO^Γ	0.60±0.05		0.50±0.05		0.51±0.05	

[a] The figures listed in columns (2) to (7) represent the percentage ratios of the band areas of the indicated phonon replicas and the associated no-phonon line. Correction has been made for the spectral dependence of the detector sensitivity for the luminescence measurements. Note that the reassignment of the TO^X phonon made in a *note added in proof* (Sec. IV) modifies these estimates of the intensities of the TO^Γ and TO^X replicas.

4. Relative Intensities of Phonon Replicas

There is reasonable agreement in the intensity ratios of the principal phonon replicas, measured relative to the no-phonon lines, between the absorption spectra discussed in Sec. III B and the luminescence spectra of excitons bound to neutral sulphur, selenium and tellurium donors, as shown in Table II. Intercomparison of the data for these two donors reveals some apparently anomalous properties, however. Simple considerations of the nature of phonon cooperation for transitions involving indirect bound excitons, based upon the discussion in Sec. IIIB of Ref. 3, leads to the following qualitative predictions.

(1) The MC replicas should exhibit approximately constant relative intensities independent of the shallow donor with which they are associated.

(2) The intensities of zone-center phonon replicas should vary in proportion to the intensity of the no-phonon line.

(3) The intensities of the MC replicas should increase monotonically (but not necessarily linearly) relative to the intensities of the zone-center replicas and no-phonon line as the binding of the exciton to the donor decreases.

Table II shows that, except for $\mathrm{Te}_{\mathrm{LA}^X}$, prediction (1) is obeyed within experimental error for the TA^X and LA^X replicas, but not for the TO^X replica. Prediction (2) is consistent with the experimental results for the LO^Γ replica, but not for the TO^Γ replica. Deviations from predictions (1) and (2) are believed to be due to interference with local-mode replicas, which are important for the heavier impurity centers (Sec. III C) (see the *note added in proof* in Sec. IV, however). Prediction (3) is in contradiction with experiment, since the binding energy of the exciton at the neutral selenium donor is 1.6 meV, or ~10%, larger than at the sulphur donor (Sec. III B 2), whereas the coupling to the MC replicas is ~5.5× larger in the selenium spectrum. Prediction (3) is obeyed when there is a more significant change in E_{Bx}, such as from $E_{Bx}\sim 0.5E_x$ to $E_{Bx}\sim 2E_x$ as has recently been shown for excitons bound to neutral centers in diamond.[24]

5. Lineshapes of Phonon Replicas

The LA^X phonon replica is $\gtrsim 4\times$ broader than the sharp symmetrical TA^X replica according to the data given in Table I, and also has an asymmetrical lineshape, with a sharp cutoff at high-phonon energies. The wave-vector interval, Δk, over which significant exciton-phonon interaction occurs is expected to be similar for the two acoustical phonon branches. The difference between the lineshapes therefore suggests that there is much less dispersion near the $\langle 100\rangle$-type zone boundaries in the frequency–wave-number curve for LA phonons compared with the curve for TA phonons. As mentioned in Sec. III A 2, the LO-LA separation at X reduces to zero as $M_1/M_2 \rightarrow 1$, and the repulsive interaction between these two branches is expected to produce a high value of d^2E/dk^2 for the LA branch near X only for relatively small value of this separation. The LO-LA separation is large in gallium phosphide for all proposed assignments (Sec. III A 2), however.

It has recently been recognised that replica S_{LA} (Fig. 1) does not belong to the sulphur spectrum, but is the MC LA^X phonon replica of a relatively weak pair of lines at 2.3147 and 2.3142 eV. Component δ_β in the 1.6°K spectrum is the MC TA^X phonon replica of these lines. Consistent with the lower value of E_{Bx} (~14 meV), the intensity of this system decreases markedly relative to the sulphur luminescence between 1.6 and 20°K (Fig. 1) and, unlike the exciton complexes discussed in this paper, the MC phonon replicas are stronger than the no-phonon lines.

The optical-phonon replicas of the S_0 and Se_0 lines are relatively symmetrical and sharp. There is a suggestion of a low-phonon-energy tail on the $\mathrm{S}_{\mathrm{LO}^\Gamma}$ replica in Fig. 1, upon which is superimposed the weak $\mathrm{S}_{\mathrm{LO}^X}$ replica. This tail, and the sharp low-energy cutoff of the $\mathrm{S}_{\mathrm{LO}^\Gamma}$ replica at the energy corresponding to the LO^Γ

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[24] D. R. Wight and P. J. Dean, Phys. Rev. **154**, 689 (1967).

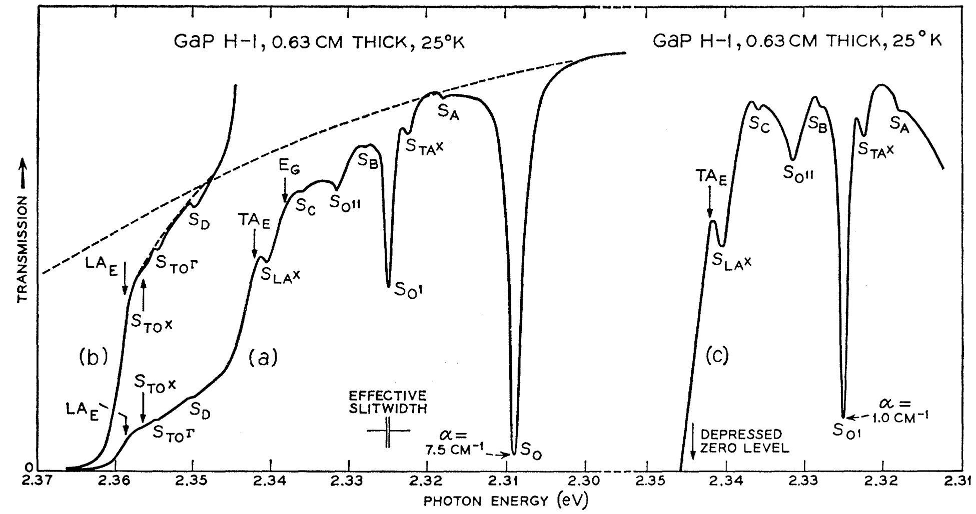

FIG. 4. The transmission spectrum near the indirect absorption edge for a single crystal of gallium phosphide which is moderately heavily doped with sulphur but still relatively strain-free. Spectra (b) and (c) were recorded using increased gain but with a Corning 5.61 filter in the optical path to reduce the distortion of the satellite lines by the sloping background spectrum shown in (2). The dashed curve in spectrum (a) denotes the energy dependence of the signal detected in the absence of the crystal. E_G and TA_E denote the calculated position of the indirect energy gap and the observed low-temperature threshold for intrinsic absorption. The notation for the absorption components is discussed in the text.

phonon[5] supports the view taken above that the energies of the LO branches diminish regularly and slowly between the center and the boundaries of the reduced zone.

B. Absorption Spectra

1. Energies of Absorption Satellites

Figure 4 spectrum (a) shows the transmission spectrum near the intrinsic absorption edge obtained from a halide-process gallium phosphide crystal which exhibits exceptionally well resolved satellite structure. Below ~2.30 eV, the signal due to the transmitted light was approximately proportional to the signal detected in the absence of the crystal indicated by the dashed curve in the main spectrum (a) of Fig. 4, and the corresponding optical absorption was very low. The satellite absorption below the first intrinsic absorption component, threshold TA_E,[4] is shown in greater detail in spectrum (c) of Fig. 4, while spectrum (b) provides a clearer view of the three extrinsic components which are superimposed on the TA_E intrinsic component.

TABLE III. Comparison of the energy intervals (in meV) between satellite and principal no-phonon lines in the absorption spectra of excitons bound to neutral donors in gallium phosphide.[a]

Satellite	Sulphur donor	Selenium donor	Tellurium donor
A	9.0±0.1		8.8±0.2
TA^x	13.4±0.2	13.2±0.2	13.2±0.2
O'	16.0±0.1	16.1±0.2	15.5±0.1
B	18.7±0.2		
O''	22.5±0.1	22.5±0.2	22.0±0.2
C	27.0±0.2		26.4±0.2
LA^x	31.3±0.2	31.1±0.2	31.1±0.3
D	40.6±0.2	40.6±0.2	40.6±0.2
TO^Γ	45.3±0.2	45.0±0.3	45.1±0.3
TO^x	47.0±0.2		

[a] All energies are in meV.

Comparison of the dashed and full-line curves in spectrum (b) of Fig. 4 indicates that there is significant broad extrinsic absorption underlying the sharp structure between S_{TA^x} and the onset of relatively strong intrinsic absorption at TA_E. The strength of this broad absorption is ~0.25 cm^{-1} at 2.335 eV, and at 2.35 eV the absorption shown in Fig. 4 exceeds that of an undoped crystal[4] by ~0.2 cm^{-1}. It is difficult to extract the exact spectral shape of the broad extrinsic absorption, but Fig. 4 suggests that it probably has a low-energy threshold near the exciton energy gap at 2.328 eV. This absorption component can be observed more clearly in luminescence excitation spectra of sulphur-doped gallium phosphide. It has similar origin to the line A_x observed in the absorption spectra of gallium phosphide containing isoelectronic nitrogen impurities, but the Coulomb forces associated with the sulphur donor center prevent observation of a sharp line at E_{gx} in this case.[25]

The absorption components S_{TA^x}, S_{LA^x}, and S_{TO^Γ} are phonon replicas corresponding to the luminescence replicas discussed in Sec. III A. Absorption component S_{TO^x} has also been labeled as a phonon replica, although the energy separation S_{TO^x}-S_0 (Table III) is significantly larger than the luminescence values given in Table I and the line is anomalously broad compared with the S_{TO^Γ} replica. This identification is therefore somewhat tentative. It is not possible to observe the

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[25] P. J. Dean, J. J. Hopfield, and D. G. Thomas, Phys. Rev. (to be published).

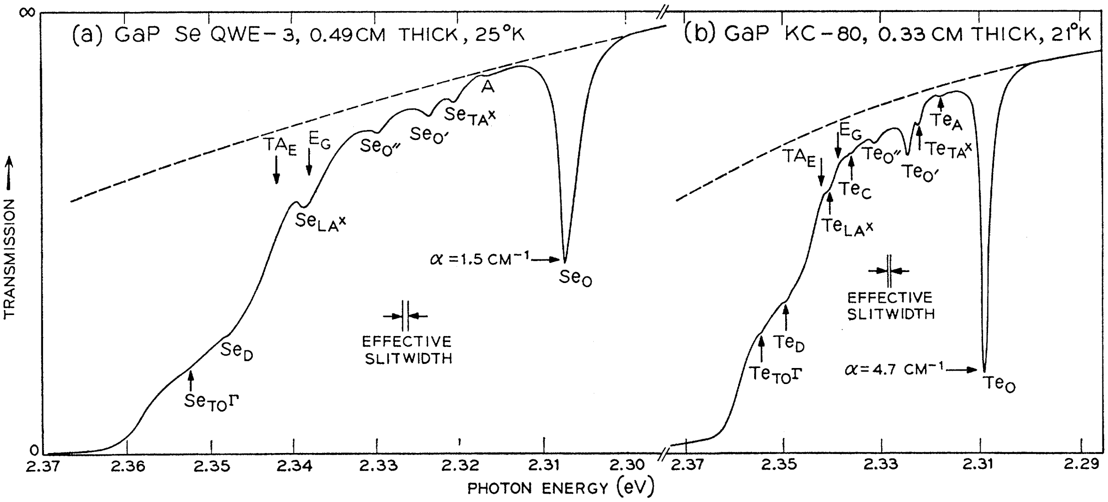

FIG. 5. Transmission spectra near the indirect absorption edge for single crystals of (a) selenium-doped and (b) tellurium-doped gallium phosphide, showing the no-phonon lines Se$_0$ and Te$_0$ together with satellite absorption lines at higher energies. The calculated position of the indirect energy gap, E_G, and the observed low-temperature threshold for intrinsic absorption, TA$_E$, are indicated. The dashed curves denote the energy dependence of the signals detected in the absence of the crystals. Note that the energy scales are different in (a) and (b).

LO$^\Gamma$ phonon replica in the absorption spectra, since it is obscured by the relatively strong LA$_E$ intrinsic component, which has a low energy threshold near 2.359 eV at 25°K.[4]

Components S$_{0'}$ and S$_{0''}$ shown in Fig. 4 are believed to represent the creation of the bound-exciton complex in various electronic excited states. Similar components are observed in the absorption spectra of excitons bound to neutral selenium and tellurium acceptors (Fig. 5). The satellite absorption components in the selenium spectrum have a very different appearance to those in the sulphur spectrum shown in Fig. 4, partly because the no-phonon Se$_0$ line is appreciably broader than S$_0$, but mainly because the intensity ratio of the phonon satellites to the excited states is much larger in the selenium spectrum (Table II). As in Fig. 4, comparison of the dashed and full curves in Fig. 5 indicates the presence of extrinsic absorption underlying the resolved satellite structure. Relative to the intensities of the principal no-phonon lines, the strength of this spectrally broad absorption (~0.3 cm^{-1} for selenium and ~1.0 cm^{-1} for tellurium at 2.34 eV) is larger in Fig. 5 than in Fig. 4, however.

The satellite structure in the sulphur and tellurium spectra is qualitatively very similar. On the other hand, Table III shows that the energy separations between the excited states and the principal no-phonon line are very similar in the sulphur and selenium spectra, but are significantly lower in the tellurium spectrum. The corresponding energy intervals for the satellites identified with acoustical-phonon-assisted transitions are, within the experimental errors, independent of the nature of the donor and consistent with the energies given from the luminescence spectra in Table I.

The very weak *A*-, *B*-, and *C*-absorption satellites can only be detected when the principal no-phonon line is strong and relatively narrow, as shown in Figs. 4 and 5b.

The stronger *D*-absorption satellite was observed for all three donors, however, and the intensity of this line was observed to vary approximately in proportion to the intensities of the TA^X and LA^X photon replicas (Table II). These observations, together with the fact that the energy interval *D*-*O* is independent of the donor (Table III), suggest that this satellite may be a phonon replica. The relative intensity of this replica in absorption is much larger than in luminescence (Fig. 1), however, in contrast to the behavior of the other phonon replicas, and its assignment is therefore uncertain. The energy of this satellite is 10–11 meV larger than the indirect energy gap. It could therefore represent an electronic excited state of the exciton-donor complex only if the donor itself is in an excited electronic state. The ionization energies, E_D, of sulphur, selenium, and

TABLE IV. Comparison of the binding energies, E_{Bx}, of excitons to neutral shallow donors with the ionization energies, E_D, of the donors in gallium phosphide.

Donor	Exciton no-phonon energy (0°K), eV[a]	Optical E_{Bx}, meV[b]	E_D, meV[c]
Sulphur	2.30955	18.9±1	107
Selenium	2.3079	20.6±1	105
Tellurium	2.3095	18.9±1	93

[a] Experimental accuracy ±0.1 meV.
[b] Calculated assuming E_{Gx} = 2.3285 ± 0.001 eV (Ref. 4), but relative values accurate to ±0.1 meV.
[c] Absolute values uncertain by ±2 meV (Ref. 26), relative uncertainty only ~±0.3 meV (Ref. 4).

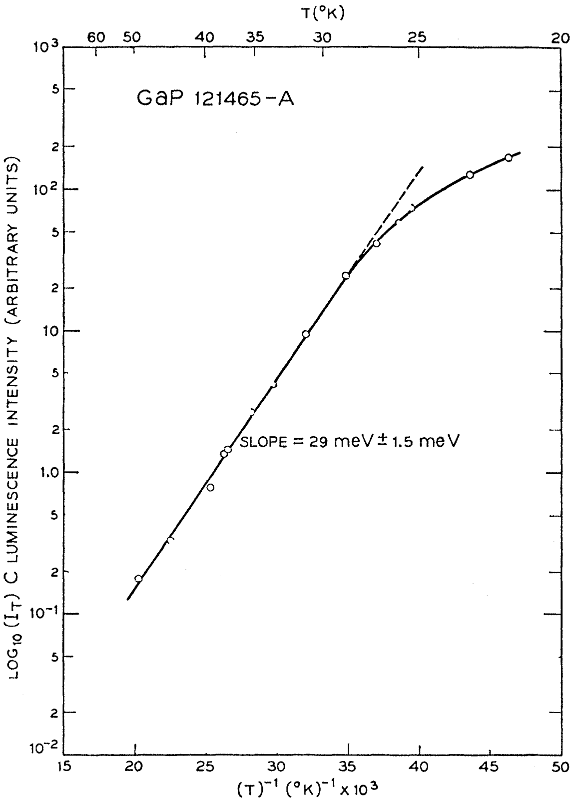

FIG. 6. The temperature dependence of the luminescence intensity of the principal no-phonon line (*C* line) in the spectrum of excitons bound to neutral sulphur donors. The axes are chosen to show the activation energy for thermal dissociation of the bound-exciton complex.

tellurium donors in gallium phosphide differ significantly[26] and are given by the equation

$$(E_D)_{\mathrm{S}} = (E_D)_{\mathrm{Se}} + (1.4\pm0.3)\ \mathrm{meV}$$
$$= (E_D)_{\mathrm{Te}} + (14.8\pm0.3)\ \mathrm{meV}. \quad (1)$$

It is therefore difficult to explain the constancy of the energy interval *D-O* shown in Table III on the hypothesis that the *D* satellite represents a no-phonon transition in which the donor center is raised to an excited electronic state.

2. *Binding Energies of Excitons at Neutral Donor Centers*

Table IV shows that there is no monotonic variation of E_{Bx} with E_D for the relatively shallow donors in gallium phosphide which are considered in this paper. The total range of variation of E_{Bx} or E_D is quite small, however, so the derivation from "Hayne's rule"[20] is not very serious. Values of E_{Bx}/E_D vary from 0.176 $\pm$0.004 for sulphur to 0.203$\pm$0.004 for tellurium. This implies that $m_e/m_h \sim 1/6$ for these donors in gallium phosphide.[27]

3. *Thermal Dissociation of the Bound Exciton-Donor Complexes*

There is at present no accurate theory for the description of the relative positions of the excited states of the exciton-donor complex. If the components S_0, $S_{0'}$, and $S_{0''}$ in Fig. 4 are regarded in terms of the creation of the exciton in three different excited states bound to the donor in its ground state, then it is significant for considerations of the stability of this complex that $S_{0''}$ occurs 3.7 meV above E_{gx}. When $E_{Bx}/E_x<1$, measurements of the thermal dissociation of similar exciton complexes[20,21,28] have shown that, as expected, the complex decays with the liberation of the exciton, since the thermal ionization energy, E_T, is equal to E_{Bx}. If $E_{Bx}/E_x>1$, as in gallium phosphide, then thermal dissociation is expected to involve the emission of a free electron.[17] Since absorption or luminescence spectra attributable to excitons bound to ionized group VI donors have not been reported in gallium phosphide, it is likely that the hole has negligible binding energy in this complex. The thermal ionization energy of the exciton-neutral donor complex should therefore be given in the high-temperature limit by the equation

$$E_T = E_{Bx} + E_x. \quad (2)$$

According to Sec. III B 2, $E_{Bx}\sim19$ meV and $E_x\sim10$ meV.[4] Thus, E_T is predicted to be ~29 meV and should be similar to the optical ionization energy. This prediction is supported by the apparent convergence of excited states $S_{0'}$ and $S_{0''}$ to an energy close to E_g. The peculiar broadened shape of component $S_{0''}$ shown in Fig. 4 suggests that it may represent the aggregate of several unresolved absorption lines, which is likely if the excited states form an energy-convergent series.

It is also possible to measure E_T directly from the temperature dependence of the integrated intensity of the bound exciton luminescence, according to the equation

$$\frac{I_T}{I_0} = \frac{1}{[1+C\exp(-E_T/kT)]}. \quad (3)$$

I_T is the luminescence intensity at temperature T, C is a temperature-independent constant and k is Boltzmann's constant. Measurements were made only above ~22°K, so that the luminescence intensity in the limit $T\rightarrow 0$°K, I_0, was unknown. Figure 6 shows that the experimental data above 28°K is adequately described by Eq. (3) in the limit $C\exp(-E_T/kT)>1$, however. The slope of the linear region between ~30 and ~50°K gives $E_T = 29\pm1.5$ meV, in excellent agreement with the prediction from Eq. (2). The curvature shown in Fig.

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[26] P. J. Dean, J. D. Cuthbert, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters **18**, 122 (1967).

[27] J. J. Hopfield, in *Proceedings of the International Conference on Semiconductor Physics, Paris* (Dunod Cie, Paris, 1965), p. 725.

[28] M. A. Yacobson, Opt. i Spektroskopiya **10**, 78 (1965) [English transl.: Opt. Spectry.—USSR **10**, 40 (1966)].

6 between 22 and 28°K arises mainly from the simplification of Eq. (3) used in plotting the data.

Use of Eq. (3), which was originally proposed for the internal quenching of centers with very localized energy levels,[29] implicitly assumes that the capture of a thermally liberated electron-hole pair by a neutral donor is unlikely. This assumption is reasonable since, besides the possibility of nonradiative recombination processes, the low-temperature luminescence spectrum of the crystal used for Fig. 6 was dominated by type-I_A[10] donor-acceptor pair transitions.

4. *Relative Intensities of Excited Electronic States*

Table V shows that the relative intensities of the electronic excited states of the exciton-neutral donor absorption spectra depend more strongly upon the donor than the energy separations listed in Table III. The broad extrinsic absorption bands underlying the resolved structure in Figs. 4 and 5, discussed in Sec. III-B 1, have been arbitrarily allowed for in the measurement of the band intensities shown in Table V. The validity of the procedure used is supported by the good agreement between the intensities of the phonon replicas measured relative to the no-phonon line shown in the comparison of the absorption and luminescence spectra in Table II.

The well-defined differences in the intensity ratios O'/O and O''/O between the sulphur and tellurium satellites indicated in Table V are of particular interest. These differences provide the most convenient method of classifying these spectra, since the no-phonon transition occurs at the same energy for these two donors within the limits of measurement (Table IV), and the small differences in the relative positions of excited state lines noted in Table III may be difficult to establish if the spectra are significantly perturbed by internal crystal strains, as is often so.

5. *Oscillator Strengths of the Principal No-Phonon Lines*

Electrical measurements on crystal GaP H-1, whose, absorption spectrum is given in Fig. 4, showed that the crystal was n-type with resistivity of 0.25 Ω cm. Assuming a mobility of 60 cm^2 V^{-1} sec^{-1} [30] this corresponds to an electron concentration of $\sim 4\times10^{17}$ cm^{-3}, which is equal to the concentration of neutral donors, N_D, at low temperatures. It is very likely that sulphur contamination is responsible for the majority of these donor centers. The shape of the S_0 line at 25°K is mainly Gaussian because of the effect of residual strain and the band area given by the product of the peak absorption coefficient and the half-height bandwidth $\alpha_{\max}\Gamma$, is $7.6\times1.5\times10^{-3}$ cm^{-1} eV. For a Gaussian absorption band, the oscillator strength, f, is given from the relation

$$N_D f = 0.87\times10^{17}\times n\times\alpha_{\max}\Gamma\,, \qquad (4)$$

where n is the refractive index at 2.31 eV, which is 3.429 ± 0.0005.[31] The local-field correction has been assumed unity in Eq. (4) in accordance with expectation for very diffuse states in semiconductors.[32] Equation (4) then gives $f\sim 8\times10^{-3}$. The total strength of the satellite bands according to Tables II and V is ~25% of the no-phonon line. Ignoring the transitions associated with the broad continuum mentioned in Sec. III B 1, the total oscillator strength of the bound exciton transition is therefore $\sim 1\times10^{-2}$.

Estimates of the carrier concentration in the selenium-doped crystals made from the reverse bias breakdown voltages at metal-crystal contacts suggest that the corresponding oscillator strength lies between 0.5×10^{-3} and 2×10^{-3}. Doping inhomogeneities were responsible for the large fluctuation in these estimates. The lower oscillator strength for the selenium exciton complex is consistent with the comments in Sec. III A 4 and with the larger relative strength of the MC replicas shown in Table II.

TABLE V. Comparison of the integrated percentage intensities of bound exciton absorption components identified with excited no-phonon electronic states measured relative to the principal no-phonon line, O, for different donors in gallium phosphide.

Excited state	Sulphur donor	Selenium donor	Tellurium donor
O'	15.0±1.0	7.0±0.5	11.0±0.5
O''	5±1	3.5±0.5	2.5±0.5

C. "Inband Resonance" Local Modes

The structure in the sulphur donor luminescence spectrum of Fig. 1 has been entirely identified with phonons selected from the lattice vibrational spectrum of pure gallium phosphide. This is the anticipated result according to the theory of local modes due to substitutional impurities of mass M_I, in a cubic crystal,[6] since the mass defect $\epsilon=1-M_I/M$ is very small (~ -0.05) for sulphur substituting for phosphorus. Only impurity vibrations within the normal range of lattice frequencies (band modes) occur for negative mass defects, and for such small values of ϵ these band modes closely follow the density of lattice states for the unperturbed crystal. As the (negative) value of ϵ increases, the local modes fall below the frequencies of the unperturbed lattice. Strong impurity bands may occur for sufficiently large (negative) values of ϵ at frequencies at which local modes would like to appear, and theory indicates that these "inband resonances" will be promi-

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[29] F. E. Williams and H. J. Eyring, J. Chem. Phys. **15**, 289 (1947).

[30] H. C. Montgomery and W. L. Feldmann, J. Appl. Phys. **36**, 3228 (1965).

[31] D. F. Nelson (private communication, 1966).

[32] D. L. Dexter, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 363.

nent in regions of low density of unperturbed lattice modes.

The relationship between ϵ and the frequencies at which the "inband resonances" should appear has been calculated for the lattice vibrational spectrum of silicon.[33] The density distribution of lattice vibrations in gallium phosphide is not known sufficiently precisely to enable a similar quantitative calculation to be made. Some qualitative predictions can be made, however, if the probable gross differences between the silicon and gallium phosphide lattice vibrational spectra are considered. Taking the three donor impurities in turn we find the following

(a) *Sulphur*, $\epsilon=-0.05$. No inband resonances are predicted, as stated above.

(b) *Selenium*, $\epsilon=-1.55$. Evidence has been quoted in Sec. III A 2 for the presence of a narrow gap between the LO and TO branches of the unperturbed lattice spectrum near 47 meV. It is likely that the strong luminescence replica $\mathrm{Se}_{\mathrm{LOC1}}$ shown in Fig. 2, occurring 46.8 meV below Se_0, is an "inband resonance" mode located in this gap. This is likely to be the principal local mode effect at this value of ϵ.[33] The appearance of a strong local-mode peak should result in a diminution of one of the bands associated with a density maximum of unperturbed modes. The $\mathrm{Se}_{\mathrm{TO}}{}^{X}$ MC replica was not resolved, but may have been obscured by the $\mathrm{Se}_{\mathrm{TO}}{}^{\Gamma}$ replica if its intensity relative to $\mathrm{S}_{\mathrm{LOC1}}$ (and $\mathrm{Se}_{\mathrm{TO}}{}^{\Gamma}$) was appreciably reduced by this effect. Indeed the $\mathrm{Se}_{\mathrm{TO}}{}^{\Gamma}$ replica is considerably stronger relative to $\mathrm{Se}_{\mathrm{LO}}{}^{\Gamma}$ than from the sulphur spectrum (Table II and Sec. IIIA2).

(c) *Tellurium*, $\epsilon=-3.12$. The spectrum of tellurium replicas in Fig. 3 is dominated by low-energy contributions, as expected for such a large (negative) value of ϵ.[33] The relative intensity of the low-energy acoustical phonon tail from Te_0 is much stronger than from S_0. There is a relatively strong broad replica $\mathrm{Te}_{\mathrm{LOC2}}$, 23 meV below Te_0, which does not appear in the sulphur spectrum, but is weakly present in the selenium spectrum of Fig. 2.

The phonon replicas shown in Fig. 3 are still preferentially selected from the available spectrum of lattice-impurity modes by the requirements of momentum conservation, however. The intensity ratio of the $\mathrm{Te}_{\mathrm{LA}}{}^{X}$ and $\mathrm{Te}_{\mathrm{TA}}{}^{X}$ luminescence replicas is $\sim 6:1$ (Table II), more than 3 times larger than for the corresponding sulphur or selenium replicas. The $\mathrm{Te}_{\mathrm{LA}}{}^{X}$ replica may be enhanced by local-mode effects, and has an unusually symmetrical shape (Sec. III A 5) and a stronger low-energy tail than would be expected from Te_0 (Fig. 3).

The relative intensities of the $\mathrm{Te}_{\mathrm{TA}}{}^{X}$ replicas are approximately equal in luminescence and absorption (Table II). The absorption spectrum does not indicate enhanced coupling to the LA^{X} phonon observed in luminescence, however neither is the local-mode $\mathrm{Te}_{\mathrm{LOC2}}$ observed [Fig. 5(b)]. This suggests that coupling to the local modes is stronger for the neutral donor center than for the exciton-neutral donor complex, whereas the coupling to the MC and zone-center phonons is similar for both states.

IV. SUMMARY

Crystals of gallium phosphide doped with group-VI donor impurities, sulphur, selenium, and tellurium show sharp-line absorption and luminescence spectra involving weakly bound indirect excitons. The spectra are dominated by no-phonon lines, whose oscillator strengths lie in the range 10^{-3} to 10^{-2}. Phonon-assisted transitions are also observed with intensities relative to the no-phonon lines in the range 1% to 13%. Phonons which conserve momentum in the indirect transition and also optical phonons of negligible momentum can be identified. The relative intensity of these two types of phonon replica depends upon the donor. The intensities of the zero-momentum phonon replicas are the more closely related to the no-phonon line intensities as expected. Marked differences between the half-height bandwidths of the LA and TA phonon replicas provide evidence for much lower dispersion in the LA than in the TA branches of the phonon spectrum of gallium phosphide near the $\langle 100\rangle$ boundaries of the reduced zone.

Additional replicas observed in absorption apparently involve excited electronic states of the bound excitons. The spectral position of these components and the thermal quenching rate of the luminescence intensity suggest that the exciton complexes dissociate by the ejection of a free electron and hole.

The luminescence spectra of the heavy donors selenium and tellurium differ from that of the almost isobaric substituent sulphur through alterations in the relative intensities of some of the phonon replicas and the introduction of other replicas. These effects were not observed in absorption. The behavior of the luminescence spectra appears to be consistent with "inband resonance" local-mode phonon structure anticipated for heavy substitutional impurities. This interpretation leads to the proposition that the LO and TO branches of the lattice vibrational spectrum of pure gallium phosphide do not cross within the reduced zone. Since this proposition is in conflict with general trends in the behavior of optical phonons in zinc blende-type semiconductors, it must be regarded as tentative at present. Bound exciton luminescence sufficiently intense for a detailed study of the weak local-mode replicas can be obtained at donor concentrations at least down to 5×10^{16} cm^{13} in gallium phosphide. Impurity concentrations of $>10^{18}$ cm^{-3} are required for the study of local modes via one-phonon infrared absorption,[33] and the infrared study can only be made for the few homopolar crystals

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[33] J. F. Angress, A. R. Goodwin, and S. D. Smith, Proc. Roy. Soc. (London) **A287**, 64 (1965).

which do not exhibit strong intrinsic absorption in this region.

Sharp-line spectra connected with excitons bound to neutral donors or acceptors which substitute for gallium ions have not yet been observed in gallium phosphide.

Note added in proof. Very recent measurements with improved sensitivity using A^+ laser excitation have revealed new bound exciton systems with no-phonon lines at higher transition energies than those discussed in the present paper. These systems apparently involve excitons bound to unknown, presumably neutral (Sec. III.A3), donors or acceptors, since the phonon replicas involve only the MC TA^X, LA^X, and TO^X phonons, quite unlike the spectra of excitons bound to isoelectronic centers.[14] The absence of additional optical phonon replicas involving, for example, the zone-center phonons is consistent with the greatly decreased relative intensity of the no-phonon lines which is, in turn, consistent with the lower values of E_{Bx} for these systems. The MC TO^X phonon can therefore be unambiguously identified in the new bound-exciton luminescence spectra, and it is necessary to partially revise the optical phonon assignments made in Table I. The revised energy of the MC TO^X phonon is 45.3±0.1 MeV, very close to the zone center TO^Γ phonon energy (45.4±0.1 meV).

Careful reexamination of the phonon replicas in the spectrum of excitons bound to neutral sulphur donors, using A^+ excitation, has shown that the replica labelled TO^Γ in Fig. 1 consists of a relatively *sharp* peak 45.3 meV below S_0 superimposed upon a significantly *broader* line. Careful low-temperature measurements have shown that the TO^Γ line is also significantly broader than the LO^Γ line in the first-order Raman spectrum of gallium phosphide[34] and analysis of the infrared reststrahl spectrum confirms that interaction with the TO^Γ mode can be described by an oscillator with a larger damping constant than is necessary for the LO^Γ mode of lattice vibration.[35] This evidence supports the identification of the broad base of the 45.3-meV luminescence replica with the TO^Γ phonon.

The sharp superimposed component is identified with the MC TO^X phonon since it has width similar to the MC TA^X replica, as in the spectra involving the relatively shallow bound excitons where only the MC TO^X optical phonon is seen, and also since, on the revised interpretation, the relative intensity variations of the phonon replicas measured for the different donors are in much closer accord with expectation than indicated in Sec. III A 4. For example, the revised intensity ratio of the TO^Γ and LO^Γ replicas in the sulphur spectrum is closer to the expected value of 2:1 (footnote 11 of Ref. 26) than indicated in Table II. The anomalously large value of the intensity ratio $\mathrm{Se}_{\mathrm{TO}}\Gamma/\mathrm{Se}_{\mathrm{O}}$ given in Table II is now readily explained, since, unlike the sulphur spectrum, most of the intensity of the 45.3-meV replica derives from coupling to the TO^X phonon for selenium. As predicted, the intensity ratios of the MC TA^X and newly identified TO^X phonons are the *same* ($\sim$2:1) for sulphur, selenium, tellurium, and the (two) new bound exciton systems which have been measured, but the relative intensity of the MC LA^X replica remains anomalously large for some systems (e.g., tellurium) possibly because of local mode effects (Sec. III C).

The abstract of this paper has been corrected to conform with the revised interpretation of the phonon replicas. The revised value of the MC TO^X phonon energy (45.3 meV) deviates even further from the most recent assignment from the second-order Raman data (48.6 meV)[16] than did the relatively inaccurate estimate from the absorption edge analysis (46.5 meV).[4] The origin of the sharp 45.9-meV phonon observed in the sulphur bound-exciton spectrum and assigned TO^X in Fig. 1 is unclear on the revised interpretation. As discussed in Sec. III C, it is unlikely to involve a local mode. Further work is necessary to establish the identity of the unassigned optical phonon replicas and the nature of the new bound-exciton complexes.

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[34] C. H. Henry and J. P. Russell (private communication).

[35] A. S. Barker, Jr. (private communication).