

Bound Excitons in GaP

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Three sharp lines *A*, *B*, and *C* are seen in absorption and fluorescence near the band edge of GaP at 20°K and below. The lines are associated with excitons bound to defects. The Zeeman splitting of the lines allow the *g* values of the holes and electrons to be determined. *A* and *B* both arise from an exciton bound to an ionized donor, the energy difference between *A* and *B* coming from electron-hole *jj* coupling. Both lines cooperate strongly with phonons, and this together with the splitting indicates a tightly bound state, yet it lies very close to the indirect exciton. Consequently *A*, *B* involves another exciton, probably made from an electron and hole both at $k=0$. Line *C* is produced by an indirect exciton bound to a neutral donor, probably sulfur. Despite the possibility of valley-orbit splitting of the conduction band, the spectrum of *C* is quite simple.

I. INTRODUCTION

GALLIUM phosphide is a cubic semiconductor with a maximum in the valence band at $k=0$ (the center of the Brillouin zone), and minima in the conduction band which are thought to lie along the $[100]$ axes away from $k=0$. The $k=0$ minimum in the conduction band is estimated to lie about 0.4 eV above the absolute minima.¹⁻³ As with other indirect-gap semiconductors, sharp-line spectra can be seen both for emission and absorption processes provided impurity states are involved, and in this paper particular attention is paid to three such lines, *A*, *B*, and *C*. These lines are quite different from the very large number of pair spectra lines which have been recently described,⁴ and also different from the broad-emission bands sometimes seen in the green and red.⁵ The analysis of the lines is chiefly concerned with the investigation of their Zeeman effects, but it is aided by comparisons which can be made with similar spectra in CdS and ZnTe. It is concluded that they arise from excitons bound to point defects. The results are of interest not only because they yield information about the lines themselves, but also because they show how minima in the conduction band which are not absolute minima can be important in fluorescent as well as absorption processes.

II. EXPERIMENTAL

The absorption and fluorescent spectra were taken with a Bausch and Lomb grating spectrograph usually using a photographic plate as the detector. For some

purposes a photomultiplier was used as a detector, and the light was then chopped. Superimposed lines from a rubidium lamp provided wavelength calibration. The photographic method is valuable because it gathers data so rapidly and because it allows rapid comparison of the spectrum from one crystal with that from another. In a similar way the effect that a magnetic field has on the many lines can be quickly assessed. The crystals were immersed in the refrigerant which was kept in a Dewar vessel between the pole pieces of a magnet which could produce a field of 31 kG. The fluorescence was usually stimulated by focusing two HB0200 high-pressure mercury arcs onto the crystal, using Corning 7-59 filters which pass light in the region 2.6 to 4 eV. Excitation by certain wavelengths was performed by selecting light from an Xenon arc with a grating monochromator. For experiments in which line *C* in absorption was quenched by red light it was necessary to use a minimum of light for the observation of *C*, and a monochromator was then used to supply a narrow band of light at the wavelength of *C*.

The crystals used in this work have been grown, usually in as pure a condition as possible, from gallium solutions by F. A. Trumbore. It is important to choose crystals which are strain free and which, as a consequence, do not show irregularities and splittings in the spectral emission lines.

III. RESULTS AND DISCUSSION

A. General

Three lines, *A*, *B*, and *C* and their associated phonon effects are discussed in this paper. Crystals showing these lines often also show at lower energies Type I or Type II pair spectra.⁴ The latter do not interfere with the observation of the Zeeman effect of *A*, *B*, and *C*, but they do fall in the same spectral region as the phonon effects of *A* and *B*, and so to study the latter the three lines should be present but the pair spectra should be

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¹ W. G. Spitzer, M. Gershenzon, C. J. Frosch, and D. F. Gibbs, *J. Phys. Chem. Solids* **11**, 339 (1959).

² H. Ehrenreich, *J. Appl. Phys.* **32**, 2155 (1961).

³ H. G. Grimmeiss, W. Kischio, and H. Koelmans, *Solid-State Electron.* **5**, 155 (1962).

⁴ J. J. Hopfield, D. G. Thomas, and M. Gershenzon, *Phys. Rev. Letters* **10**, 162 (1953).

⁵ M. Gershenzon and R. M. Mikulyak, *Solid-State Electron.* **5**, 313 (1962).

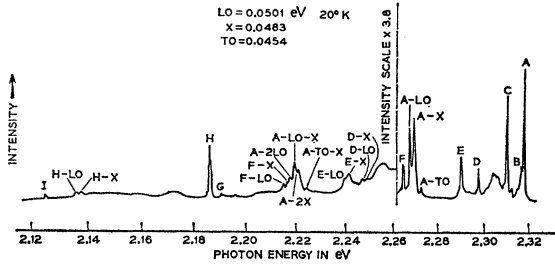


FIG. 1. Fluorescence from a type *O* crystal at 20°K. The lines *A*, *B*, *C*, *D* ..., etc., are no-phonon lines. Several of these lines are multiplets and at lower temperatures there is a redistribution of strength; thus at 1.6°K *B* is much stronger than *A*. Some of the no-phonon lines are repeated at lower energies and these can be accounted for in terms of three phonon energies which have been marked.

absent. Fortunately, such crystals called Type *O* were obtained when the growing system was exposed to air. The reason for the absence of the pair spectra in these crystals is not clear.

Figure 1 shows a Type *O* spectrum taken at 20°K. *A*, *B*, and *C* are very sharp lines (measured half-width about 5×10^{-5} eV), and in suitable crystals sharp absorption lines are seen at precisely the same wavelengths (although the *B* line is much weaker than the *A* line). These lines are consequently no-phonon lines, which are associated with impurities since they vary in intensity from crystal to crystal. (In view of the positive identification of *A*, *B*, and *C* as no-phonon lines, some of the conclusions drawn in a previous paper⁶ concerning these and other absorption lines must be reconsidered.) Other sharp lines occur in the spectrum and have been marked *D*, *E*, *F*, *G*, and *H*; these are no-phonon lines arising from other centers and will not be further discussed.

There remain numerous somewhat broader peaks which can be derived from no-phonon lines by subtraction of one of three phonon energies, or combinations of these energies. The strongest of these peaks are those derived from line *A*. Also broader phonon bands occur, some of which doubtless involve acoustic phonons. Two of the three phonon energies, $LO = 0.0501$ eV and $TO = 0.0454$ eV, are in excellent agreement with the *LO* and *TO* energies at the center of the Brillouin zone, which were obtained from the infrared spectrum of GaP.⁷ The third phonon energy, $X = 0.0483$ eV, does not correspond to an identified phonon energy, but it happens to fall close to half the energy of an infrared combination band⁷ (at $784 \text{ cm}^{-1} = 0.0972$ eV), which was tentatively ascribed to a three phonon process.

The main phonon effects are derived from *A* (and *B*), rather than *C*. This is shown by the identities described in the last paragraph and also by the following observations:

(a) As the temperature is lowered from 20 to 4.2 to 1.6°K, *A* loses and *B* gains strength. There are then corresponding changes in the phonon lines which exactly parallel the changes in *A* and *B*.

(b) At 1.6°K *A* is very weak and *B* is strong. In a magnetic field of 31 kG, *B* undergoes a large splitting (as described below), and due to thermalization in the multiplet most of the energy is associated with the lowest line, so that the net result is to shift the radiation to lower energies. When this happens all of the phonon peaks mentioned above shift similarly. The shift in line *C* is much smaller and no corresponding phonon shifts can be seen.

It is concluded that the interactions of line *C* with phonons is much weaker than that of *A* and *B*.

B. Discussion of Phonon Effects

An understanding of the origin of phonon-cooperative effects permits the drawing of some qualitative conclusions from these effects. At zero temperature, an optical transition between two bound states is expected to consist of a sharp "no-phonon" line and a phonon-cooperative wing lying to higher (lower) energy in absorption (emission). There are two extremes of phonon cooperative effects. In the "allowed transition" extreme, the optical transition in a rigid lattice has an oscillator strength which is related to the binding energies involved. In a real (nonrigid) lattice, the change in equilibrium lattice configuration between initial and final states results in the statistical emission of phonons in the transition. The "rigid-lattice" oscillator strength is shared over all possible phonon final states. The greater the difference in equilibrium lattice configuration between initial and final states, the more probable one-phonon transitions become relative to no-phonon transitions, the more probable two-phonon transitions become relative to one-phonon transitions, etc. When the coupling constant between phonons and free carriers is low (as in GaP), strong phonon cooperation is evidence of strong binding of either the electron or hole before recombination. Good examples of such phonon cooperative effects are exhibited by⁸ CdS and⁹ ZnTe.

In the "forbidden-transition" extreme, the optical transition in a rigid lattice has no oscillator strength. In a nonrigid lattice, the phonon-cooperative wings gain oscillator strength through the phonon-induced strain. The zero-phonon line will be lacking. An example of such a transition is the radiative decay of a free thermal exciton in Si at low temperatures. In this case, the indirect band gap necessitates the cooperation of a phonon of particular wave vector in order to conserve momentum. An exciton weakly enough bound to a defect will have the same selection rules and phonon cooperation as a free exciton. As the binding energy of

⁶ M. Gershenson, D. G. Thomas, and R. E. Dietz, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 752.

⁷ D. A. Kleinman and W. G. Spitzer, *Phys. Rev.* **118**, 110 (1960).

⁸ D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **128**, 2135 (1962).

⁹ R. E. Dietz, D. G. Thomas, and J. J. Hopfield, *Phys. Rev. Letters* **8**, 391 (1962).

TABLE I. Degeneracies of the ground states of simple complexes for simple bands (twofold spin degeneracy only) and GaP in the effective mass approximation, neglecting valley-orbit coupling and electron-hole and hole-hole spin-spin interactions. Degeneracies for GaP are listed for three valleys at the 100 direction zone boundary, and in parentheses for the possibility of 6 (100) valleys in the interior of the zone. "Simplified GaP" is equivalent to GaP with a simple conduction band, a good approximation for states involving donors (see text).

	Donor degeneracy	Acceptor degeneracy	Exciton and charged donor	Exciton and charged acceptor	Exciton and neutral donor	Exciton and neutral acceptor
Simple bands (CdS)	2	2	4	4	2	2
GaP bands	6 (12)	4	24 (48)	24 (48)	60 (264)	36 (72)
Simplified GaP	2	4	8	?	4	?

an exciton to the defect increases, the wave function spreads in \mathbf{k} space, some component of direct band-gap wave function can be mixed in, and the no-phonon transition becomes allowed. In this case, one expects (and finds) the strength of the one-phonon transition relative to the no-phonon part at first to *decrease* with increasing binding.

In the extreme of allowed transitions, phonon cooperation is approximately equally strong for all phonons of wave vector less than $1/a$, where a is the smallest characteristic radius of the binding of the electron and hole. In the extreme of transitions forbidden because of an indirect band gap, the dominant phonons are those whose wave vectors characterize the indirect gap.

Thus, the absence of strong phonon cooperation with line C is consistent with it being an "indirect" transition with moderately tight binding. On the other hand, line A, B with strong phonon cooperation, particularly with phonon wings not confined solely to one wave vector, is consistent with a tightly bound, direct transition.

C. Theory of Bound Excitons in GaP

The simple theoretical considerations necessary to understand the binding energies, Zeeman effects, and optical selection rules for simple bound excitons in CdS⁸ (a direct band gap, hexagonal semiconductor) are not quite adequate in GaP. In the case of CdS, simple considerations of hydrogen molecule analogs were sufficient to estimate the ground-state energy and orbital wave function, all remaining degeneracy or fine structure being due to electron and hole spin. The fourfold degeneracy of the valence band and the three- (or six-) valley structure of the conduction band in GaP greatly complicate the problem. A comparison of the degeneracies of the estimated ground state of various simple complexes in the effective mass approximation (including the effect of the exclusion principle) is shown in Table I. Remembering that no state in a cubic crystal is more than fourfold degenerate for symmetry reasons, we conclude that the possible fine structure of the ground state is prodigious. A complete analysis of the symmetry possibilities is straightforward and unrewarding.

The chief cause of complications in the energy level systems under consideration is the three- (or six-) valley nature of the conduction band. It is known that

valley-orbit coupling will split many-valley degeneracies, that theoretically for an attractive valley-orbit coupling the singlet (twofold spin degenerate) state lies lowest, and that in silicon (a close analog to GaP) all donors which have been investigated by spin resonance have this property. Furthermore, valley-orbit couplings are sufficiently large that (at temperatures of 20°K and below) only this twofold degenerate state, of all possible donor states, need be considered as a possible initial state for optical processes. The same consideration should apply for all ground-state configurations involving a donor and one electron (plus various holes).

The optical absorption of a transition in which an exciton is made at an ionized donor might conceivably have several components representing different valley orbit final states for the electron. In the GaP band structure, such transitions making an *indirect* electron are expected to obtain their oscillator strength by virtue of the (small) component of $\mathbf{k}=0$ electron wave function mixed into the bound state. Only the *symmetric* valley-orbit state has such a component.

When two indirect electrons are placed on a single donor, the total energy of the system depends on whether the electrons are in the same or different valleys, since the valleys are anisotropic. This effect tends to keep the electrons in different valleys. This orientational energy is small, amounting to only about 5% of the Coulomb repulsion of the two electrons. An attractive central cell potential, on the other hand, favors placing both electrons in the symmetric (singlet) superposition of valley states. Even a modest central-cell potential is sufficient to overcome the orientational energy, so both electrons are expected to occupy the singlet valley-orbit state. Neglecting configuration mixing, the optical decay must leave the donor in the singlet state.

These considerations indicate that optical properties at low temperatures due to the binding of excitons to charged or neutral donors will show no explicit many-valley effects. This is the "simplified GaP" of Table I. The optical lines will have the same multiplicity and magnetic splittings as they would for a simple conduction band.

For this "simplified GaP," the ground state of a neutral donor has "spin" $\frac{1}{2}$ and splits with an isotropic electron g value. The exciton bound to a donor has

“spin” (due to the hole) $\frac{3}{2}$ and the hole g value. The optical-selection rules appropriate are the usual atomic ones. The ordering of valley-orbit energy levels and the source of strength indicate that at low temperatures this one transition should predominate both in absorption and emission.

Categorical statements about the optical effects expected for an exciton bound to a neutral or charged acceptor in GaP are more difficult. In this case, it is not clear that there will be an appreciable central-cell correction for the electron. If there is a central-cell potential, it may well be repulsive for the electron. In this case the electron would occupy (nonsinglet) valley-orbit states. Magnetic splittings will be correspondingly complicated.

The absorption spectrum for the binding of an exciton to a charged acceptor will contain *one* principal allowed absorption line. This transition is not necessarily to the lowest state (see previous paragraph), so the form of the emission at low temperatures is not necessarily the same as the absorption.

The absorption spectrum for the binding of an exciton to a neutral acceptor will contain two lines of approximately equal strength. The origin of these two lines are the two different ways of putting a pair of $j=\frac{3}{2}$ particles into a spin antisymmetric wave function. An analog of such a splitting has been observed in CdS. Again, little can be said *a priori* about the emission.

D. Line C

Results in Zero Magnetic Field

Line *C* has no observable phonon wings, which is in marked contrast to lines *A* and *B*. It is concluded that *C* represents the decay of a rather weakly bound state. *C* lies at 2.310 eV and the lowest energy exciton (made from a hole, and an electron in the indirect conduction band minima) lies at 2.315 ± 0.005 eV.⁶ (In going from 20 to 1.6°K the band gap increases in energy by only about 10^{-4} eV.) Thus, *C* probably represents an indirect exciton bound to a defect with an energy of about 0.005 eV. With such a small binding energy the exciton must be bound to a neutral center, either a donor or acceptor.⁸ (Donor and acceptor binding energies in GaP are generally in the range 0.03–0.15 eV,⁵ while the indirect exciton is estimated to have a binding energy of 0.01 ± 0.005 eV.)⁶ As explained in Sec. III C, two allowed nondegenerate optical transitions are expected for the formation of an exciton bound to a neutral acceptor. Since only one absorption line is seen at *C*, it seems likely that an acceptor is not involved. It is also shown in Sec. III C that a single allowed transition can occur at a neutral donor provided the donor is in its “singlet” state. Thus, *C* probably arises from a neutral donor the ground state of which is singlet.

The conclusion concerning a *neutral* center is supported by the observation that the intensity of line *C*

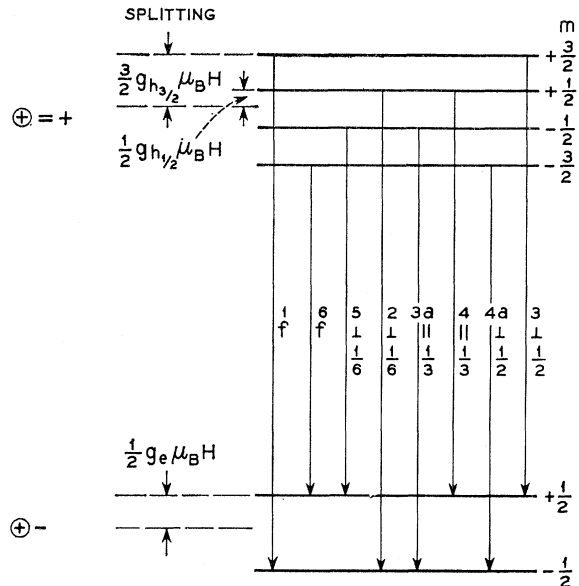


FIG. 2. Schematic energy levels for line *C* involving an exciton trapped at a neutral donor. All the electrons are derived from the indirect conduction band minima, but are in the “singlet” state, and so the two electrons in the excited state are paired off. The lines are numbered to fit the scheme of Fig. 4 where it is assumed that 3 and 3a, and 4 and 4a are so close that experimentally they are indistinguishable. The expected polarizations and strengths are indicated, *f* indicating a forbidden line. μ_B is the Bohr magneton and H the magnetic field.

in absorption can be diminished by irradiating the crystal with red and infrared light. It is necessary to use a minimum of band-gap light in this experiment as this tends to form neutral centers via free holes and electrons, whereas the weakly absorbed red light tends to ionize the donors and acceptors. Very similar effects have been observed for lines involving excitons bound to neutral donors and acceptors in CdS.⁸

In addition, previous experiments have demonstrated a correspondence between the intensity of the absorption line *C* and the concentration of neutral donor sulfur atoms present in the crystal.⁶

Line C in a Magnetic Field

If line *C* represents an exciton in its singlet state bound to a donor in its singlet state, then the energy levels in a magnetic field will be as shown in Fig. 2. The excited state will split as a result of the hole degeneracy only, since the two similar electrons must be paired off by the exclusion principle. It should be possible to account for the observed splittings in terms of this scheme.

At 20°K in a magnetic field line *C* as seen in fluorescence splits into a well defined quartet as shown in Fig. 3. The inner pair of lines are not strongly polarized, but the outer pair occur with the E vector polarized perpendicular to the magnetic field ($E \perp H$). In crystals which contain a small residual strain (as may be judged by the splitting of *C* at zero magnetic field), an extra

pair of very weak and diffuse lines may be seen lying on either side of the quartet. It is found that if the crystal is rotated in a magnetic field of 31 kG, the positions of the lines change; these results, concerning g -value anisotropies, are discussed elsewhere.¹⁰ As the temperature is lowered the intensities of the lines change indicating that thermalization of the system among the levels of the excited state is taking place. A representation of these results is given in Fig. 4. Lines 1 and 6 are clearly forbidden transitions. It is to be particularly noticed that at very low temperatures the fluorescence collapses onto line 4.

The energy level scheme of Fig. 2 predicts a total of six allowed transitions with the polarizations indicated, and at high temperatures with the relative strengths indicated. Since only four allowed transitions are seen, it is clear that if the proposed energy scheme is correct accidental coincidence must occur at two of the lines. Lines 3 and 4 are unpolarized and so most probably the coincidences occur here. This means that lines 3 and 3a (see Fig. 2) have one energy and lines 4 and 4a have another. The g values of the various lines then become:

Lines	g Value
3, 4	$ g_{h_{1/2}} - g_e = g_e - 3g_{h_{3/2}} $
2, 5	$ g_{h_{1/2}} + g_e $
1, 6	$ 3g_{h_{3/2}} + g_e $

The symbols are explained in Fig. 2. The splitting of lines 1 and 6 cannot be accurately determined, but from the splittings of 2 and 5, and 3 and 4, and the relations just quoted, the following values are determined for $H \parallel [111]$:

$$\begin{aligned} g_e &= 1.89 \pm 0.10, \\ g_{h_{1/2}} &= 1.12 \pm 0.10, \\ g_{h_{3/2}} &= 0.93 \pm 0.04. \end{aligned}$$

The relative intensities of lines 2, 3, 4, and 5 can be readily calculated at low temperatures assuming that thermal equilibrium is reached in the excited state. The results of these calculations are in qualitative accord with observation. The energy-level diagram shows how

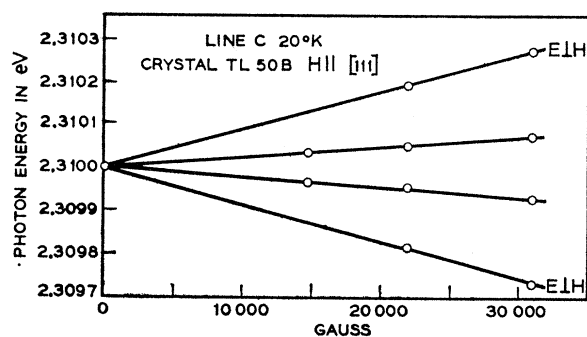


FIG. 3. The Zeeman splitting of line C for $H \parallel [111]$. The outer pair of lines are polarized with $E \perp H$, but the inner lines are not strongly polarized.

¹⁰ Y. Yafet and D. G. Thomas, following paper, Phys. Rev. 131, 2405 (1963).

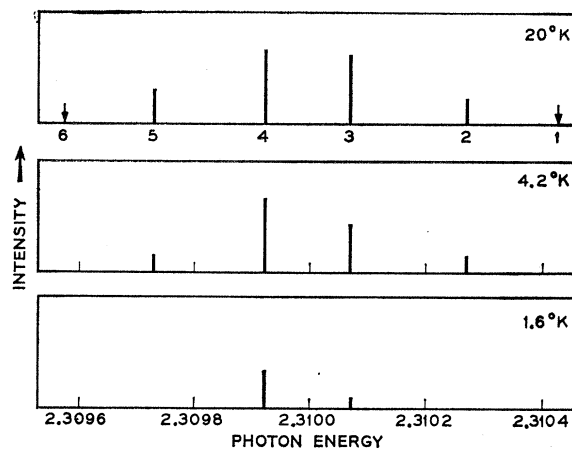


FIG. 4. Observed intensities of the lines derived from C at 31 kG at various temperatures. The intensities are taken from a photographic plate and are approximate. Lines 1 and 6 are only seen weakly in strained crystals. At very low temperatures the lines become weak compared to the background radiation.

at low temperatures the transitions collapse to a single allowed line at position 4. It is to be noticed that if the transition were occurring at a neutral acceptor so that there were an unpaired electron in the excited state, the multiplet would collapse to a triplet at low temperatures.

We conclude that both the magnetic and nonmagnetic evidence shows that line C arises from an exciton which includes an electron from the indirect conduction band minimum in association with a neutral donor center. The chemical evidence indicates the donor may be sulfur, although it has not been proved that other donors may not give a very similar line.

E. Lines A and B

Two lines are frequently seen together in fluorescence which have been called lines A and B, with A lying 0.8×10^{-3} eV above B. At 20°K, A is much stronger than B, but at 1.6°K the reverse is true. Near 2.5°K, the strengths are comparable. [It should be noticed that kT at 2.5°K (0.216×10^{-3} eV) is considerably smaller than the separation between A and B.] This variation of relative intensity is caused by temperature alone, and is independent of the crystal, and thus shows that A and B arise from the same center in the lattice. In suitable crystals, A can be seen in absorption as a strong sharp line, while B occurs as a very weak line. As explained above, in marked contrast to line C, lines A and B have associated with them phonon effects. These are illustrated in Fig. 1.

There is a similarity between this transition and one seen in ZnTe.⁹ In ZnTe the transition occurs 0.4 eV below the (direct) band gap and consists of two lines separated by 1.7×10^{-3} eV. There is associated with it phonon structure consisting of broad bands and sharp peaks which may be related to phonon energies. Except for the fact that in ZnTe the coupling to the phonons

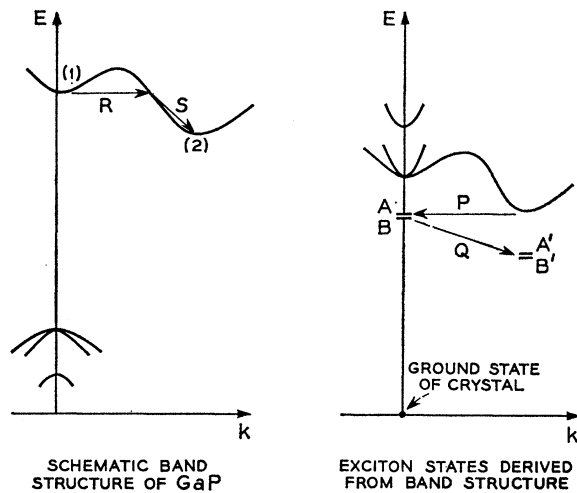


FIG. 5. Schematic diagrams of the band structure and of the excitons in GaP. Various processes are illustrated which are discussed in the text.

is stronger, so that the strongest emission lies at an energy approximately 4 phonons less than the no-phonon line, the phonon effects in GaP and ZnTe are very similar. The transition is ascribed to an exciton bound to an ionized donor or acceptor. The splitting of the line arises from the energy difference between the $J=1$ and $J=2$ states formed by the combination of a $j=\frac{3}{2}$ hole and a $j=\frac{1}{2}$ electron to form the bound exciton. Since the exciton is bound to an ionized center, there can be no possibility of one particle pairing off with a similar particle, as can happen when an exciton binds to a neutral center. The allowed transition, seen strongly in absorption, is to the higher energy $J=1$ state, the forbidden to the $J=2$ state. The $J=2$ state is seen in fluorescence at low temperatures when kT is small compared to the $J=1, J=2$ energy separation, so that the system is compelled to spend most of its time in the $J=2$ state. The binding energy of an exciton to an ionized center may be thought of as being derived in the following way. If the center is an ionized donor it will first bind an electron yielding the donor binding energy, and to the neutral donor is now added a hole liberating a smaller amount of energy. The total energy of the state is thus the band-gap energy less somewhat more than the donor binding energy. Analogous arguments apply to ionized acceptors. Thus, in ZnTe we conclude that the ionized center has a binding energy of between 0.3 and 0.4 eV.

It is therefore concluded that in GaP the splitting of A and B , and the phonon structure, indicate that this state should lie at least a tenth of an eV below its corresponding band gap. Now A lies at 2.317 eV, whereas the lowest energy intrinsic exciton lies near 2.315 eV.⁶ Therefore, this exciton has a binding energy of only about 0.01 eV. Since all known donors and acceptors have larger binding energies, it is clear that A, B is not derived from the minimum-energy band gap but

from an exciton which derives its electron from a higher lying minimum in the conduction band. The $k=0$ minimum lies 0.4 eV above the indirect minimum so that it is probably this minimum which is involved. The optical transition is then direct and will have a greater oscillator strength than comparable indirect transitions. Support is lent to this argument by the observation that in "undoped" crystals the strongest line seen in absorption is line A . It is not expected that the center responsible for A is present in abnormally large concentration. [It cannot yet be definitely stated that A does not arise from other minima such as (111), although it seems less likely. Fluorescent lifetime measurements, and the effects of a uniaxial stress on the spectra, should decide the point.]

The fact that fluorescent decay occurs from A and B does not imply that there is a significant number of free electrons in the direct conduction band minimum [designated as (1) in Fig. 5]. The state might, for example, become excited by the initial formation of an indirect exciton and the trapping of this by process P (see Fig. 5). Since this step involves only a very small gain or loss of energy, and so the absorption or emission of one phonon, it will go very easily. The change of crystal momentum is readily taken up by the lattice as an impurity center is involved. The subsequent optical decay will also be favorable since it is also a process that does not involve phonons. It is clear that indirect excitons, or at least free electrons at the bottom of valley (2) are involved in the excitation process, since, although there must be many states derived from valley (1) above A and B , no fluorescence is seen above A and B . Transitions above A and B may, however, be seen in absorption provided they are not broadened by short lifetimes, and not obscured by indirect intrinsic absorption.

The reason that the free electrons can rapidly transfer from valley (1) to valley (2) is that a single-phonon

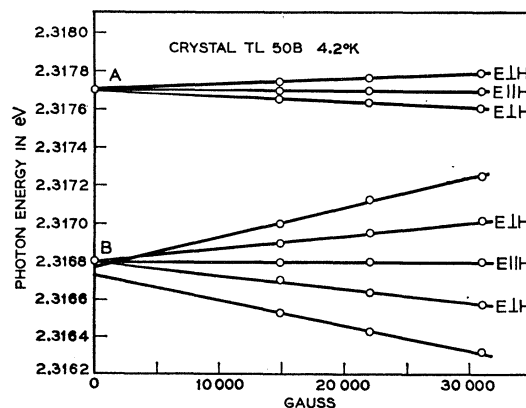


FIG. 6. The Zeeman splitting of lines A and B for $H \perp (110)$ and $\parallel (111)$. The outer pair of lines of B are diffuse and the fact that they do not extrapolate to the $H=0$ point may not be significant. The polarizations for B are only qualitative. As the temperature is lowered A becomes weaker compared to B and the lower energy lines of each multiplet gain strength.

process can be involved in step R , and the subsequent cascading down the conduction band, process S , can also take place easily. It is the absence of such a continuum of states that slows down process Q to any analogous states, A' and B' which might be imagined under valley (2).

We assume, therefore, that A and B arise from a direct exciton bound to an ionized particle, in close analogy to ZnTe. It is now possible to show that the center is derived from an ionized donor rather than an ionized acceptor. At present no such distinction can be made for ZnTe. The argument is as follows: It is an experimental fact that the fluorescence of A and B can be stimulated by light with a photon energy only 0.08 eV above the energy of A and B , and that the efficiency of this process is not greatly altered as the photon energy is increased. We have seen that the phonon structure and the fact that the state arises from an ionized center show that the center is tightly bound, yet it can be made from, and also radiates approximately at, the energy of a weakly bound exciton. This is only possible if, as has been suggested, one of the particles changes in such a way that it is derived from a higher lying minimum; since it is far removed from its band edge this must be the tightly bound particle. Since the fundamental assumption is that it is the conduction band which has the alternate minima, the particle which changes valleys must be the electron. The only center to which an electron can be tightly bound is an ionized donor and so this must be responsible for A and B . Alternatively, one can arrive at a similar conclusion by imagining an exciton tightly bound to an ionized acceptor being made from the indirect exciton; it would have an energy level below the indirect exciton by an amount at least as great as the acceptor binding energy. In fact, AB radiates almost at the level of the indirect exciton. The point is that although an ionized acceptor and a direct exciton can give a level at A and B , it could not be formed from the indirect exciton, and yet this is observed to be the case.

The difference in energy between the direct and indirect conduction band minima is not known precisely, and so the binding energy of the donor involved in A and B is not known precisely. However, as quoted above, the energy is estimated to be 0.4 eV, which is quite comparable to the value of 0.4 eV for the similar transition in ZnTe. The donor might be a P vacancy which, in analogy to the F centers in the alkali halides, is expected to have a large binding energy because of the large void left in the lattice. However, it might be identified with the donor of binding energy 0.4 eV previously associated with oxygen.⁵

F. Simultaneous Presence of A , B , and C

A and B are believed to arise from a deep ionized donor, while C arises from a shallow, neutral donor. At equilibrium, therefore, it is not expected that both lines would be present simultaneously. However, non-

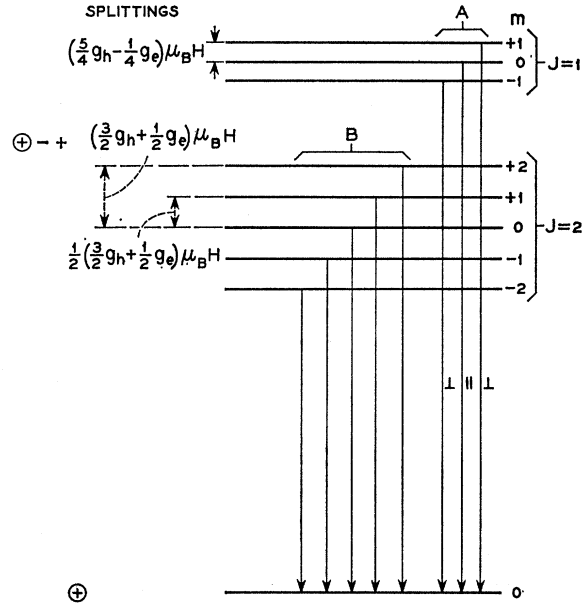


Fig. 7. Schematic energy levels for lines A and B involving an exciton trapped at an ionized donor. The splittings have been expressed making certain simplifying assumptions about the g values which are approximately true and which are discussed in the text.

equilibrium conditions can be brought about by incident radiation which can make holes and electrons or ionized centers, depending upon its frequency. An example of this was provided by the quenching results of line C quoted above. This "pumping" action by band-gap light is probably responsible for the simultaneous presence of the lines as seen in fluorescence. In absorption much less intense light is incident on the crystal and a closer approach to equilibrium may be expected, and in general it is true that if C is strong (as for instance in sulfur-doped crystals), then A and B are absent or very weak, and if A and B are strong ("undoped" crystals), then C is absent or very weak.

G. Lines A and B in a Magnetic Field

The Zeeman data of lines A and B confirm the model discussed in the previous section. As illustrated in Fig. 6, the allowed $J=1$ state splits into a polarized triplet, and the forbidden $J=2$ state into a quintet. The polarization of the triplet is as expected with the outer members polarized with $E \perp H$, the inner with $E \parallel H$. The central line of the forbidden quintet is strongly polarized with $E \parallel H$, and the adjacent pair of lines are polarized with $E \perp H$. The highly forbidden outer pair of the quintet is rather diffuse. Both the triplet and quintet show simple thermalization effects. As the temperature is lowered the lower energy lines of the multiplets become stronger and, from the change of ratio of strengths between two lines, "thermal g values" may be estimated which are found to be in agreement with the observed g values. Thus, the splitting arises

completely from the excited state, the ground-state splitting being zero. These observations are all explained by the energy-level scheme presented in Fig. 7. The diagrams have been labeled with g values which are expected, if it is assumed that (a) all g values are isotropic and for the hole $g_h = g_{h_{3/2}} = g_{h_{1/2}}$, and (b) the crystal field splitting of the $J=2$ state is negligible. (These assumptions are approximately true; deviations are discussed elsewhere.¹⁰) Accordingly, we deduce from these lines for $H \parallel \langle 111 \rangle$,

$$g_e = 2.02 \pm 0.12,$$

$$g_h \approx 0.99 \pm 0.06.$$

IV. SUMMARY AND CONCLUSIONS

In this paper, three lines A , B , and C , which occur in the very complex low-temperature spectra of GaP, have been singled out for attention. They are quite unconnected with the many lines which arise from the pair spectra⁴ since crystals occur (Type O) in which A , B , and C are present but the pair spectra absent.

A and B , separated by 0.8×10^{-3} eV, are derived from the same center since the fluorescent intensity ratio between the two lines is strongly temperature-dependent, favoring the low-energy line B at very low temperatures. In absorption, A is much stronger than B , and it is concluded that A is an allowed transition, B a forbidden transition. There is considerable phonon cooperation with A and B which indicates that the state is tightly bound. These observations may be understood in terms of an exciton bound to an ionized center, in which the splitting of A and B is the j, j interaction energy between the hole and electron. The evidence, together with an analogous transition in ZnTe, indicates that the exciton is bound with an energy of a tenth of an eV or more. Yet A and B lie very close to the lowest energy intrinsic exciton which includes an electron from the indirect ($k \neq 0$) conduction band minimum. Consequently, A and B cannot be derived from this exciton and it is concluded that it is probably derived from an exciton involving an electron from the higher

lying $k=0$ minimum. Arguments may then be introduced to show that an ionized donor rather than acceptor forms the ground state of the transition. The Zeeman effect of A and B confirms that the j, j interaction dominates the zero-field splitting, and gives the g values of the hole and electron involved.

Line C , which lies about 5×10^{-3} eV below the indirect intrinsic exciton, occurs as a singlet and no observable phonon effects are connected with it. It is, therefore, a weakly bound state derived from the indirect exciton. It is particularly interesting that the possibility of valley-orbit splittings associated with the $k \neq 0$ electron does not lead to a complex spectrum. This is because the singlet states lie lowest in both the ground and excited states and that the allowed transition occurs between such states. The Zeeman effect and its associated thermalization results show that the ground state consists of a neutral donor and that the only unpaired particle in the excited state is a hole. Thus, the g values of the electron and hole may be determined and also the anisotropies of these quantities. The method thus provides one of the few ways of determining the magnetic levels of the hole in an unstrained cubic semiconductor.

In addition to the lines described here, and to the pair spectra, many other lines have been seen in fluorescence from GaP. Some of these are probably similar to A , B , and C , but others probably arise from excitons associated with neutral acceptors and donors and ionized acceptors. It would clearly be of value to be able to purify the crystals and then introduce impurities under controlled conditions, for exciton spectroscopy provides a method of gaining knowledge both concerning the impurity states themselves and the mechanism of the radiative recombination of holes and electrons.

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