

served width W_O as

$$W_O^2 = W_I^2 + W_D^2.$$

These values are summarized in Table I along with the expected half-width calculated from Eq. (1) using the mean of the two slit-width measurements. The agreement is within experimental uncertainty for all cases.

These Fraunhofer diffraction observations indicate that the neutron wavefront as it approaches the slit must be coherent over a transverse width at least that of the largest slit studied, namely 21 μ . This is interest-

ing when considered in light of the conclusions drawn from Pendellosung fringe observations reported separately,⁵ where the coherence length of neutron wave packets was established as being at least 0.3 μ . Thus the coherence volume of a neutron wave packet must be considered to be very extended relative to the de Broglie wavelength scale.

The author appreciates many helpful discussions with R. Nathans and design considerations and skilled craftsmanship by F. Langdon, W. Lenz, A. Roebuck, and A. D'Addario.

⁵ C. G. Shull, Phys. Rev. Letters **21**, 1585 (1968).

Interimpurity Recombinations Involving the Isoelectronic Trap Bismuth in Gallium Phosphide

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A new type of pair spectrum involving the radiative recombination of holes bound to Bi isoelectronic traps with electrons bound to remote shallow group-VI donors has been observed in GaP. The existence of these spectra proves that an isoelectronic impurity forms a stable trapping state for a single electronic particle. The binding energy of this state can be calculated from the positions of the pair spectra, and is 40 ± 1 meV for the Bi hole trap in GaP. The prominent phonon sidebands in the Bi-donor pair spectra and in the luminescence spectrum due to recombination from the $J=1$ Bi bound exciton state are similar, although the latter contains more detailed structure. The relatively large increase in the transition energy with decreasing pair separation r , characteristic of donor-acceptor pair spectra, is not observed in the Bi-donor pair spectra, where the first-order Coulomb interaction is zero because the Bi trap is neutral before the hole is captured. Instead, the Bi-donor pair transition energy *decreases* slightly with decreasing r as a result of the electrostatic polarization interaction between the charged Bi trap and the neutral donor. The low-temperature time decay of both the Bi-donor and donor-acceptor pair spectra in GaP are slow and nonexponential, confirming that remote Bi-donor pairs of widely variable separation are involved. The decay time of the total luminescence is dramatically reduced, and the slow-decaying Bi-donor pair luminescence is quenched relative to the fast Bi-exciton luminescence, when the temperature is increased above $\sim 15^\circ\text{K}$. These changes are attributed to the phonon-assisted tunneling of electrons from the donors to Bi traps already filled by holes.

I. INTRODUCTION

THE ability of isoelectronic impurities to produce bound exciton states was first recognized in GaP.¹ Only certain isoelectronic impurities can do this in a given semiconductor. For example, N¹ and Bi² atoms in GaP trap excitons with localization energies,³

respectively, ~ 11 and ~ 97 meV. No bound exciton state occurs when some of the P atoms are replaced by As atoms, however. Bound exciton (B.E.) states associated with isoelectronic impurities have now been discovered in several different semiconductors, including ZnTe⁴ and CdS.⁵ Such states have not yet been reported for isoelectronic impurities on the cation

¹ D. G. Thomas, J. J. Hopfield, and C. J. Frosch, Phys. Rev. Letters **15**, 857 (1965).

² F. A. Trumbore, M. Gershenson, and D. G. Thomas, Appl. Phys. Letters **9**, 4 (1966).

³ The energy difference between the free and bound indirect exciton transitions.

⁴ J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters **17**, 312 (1966).

⁵ A. C. Aten, J. H. Haanstra, and H. de Vries, Philips Res. Rept. **20**, 395 (1965); J. D. Cuthbert and D. G. Thomas, J. Appl. Phys. **39**, 1573 (1968).

site in compound semiconductors, or for isoelectronic impurities in the group-IV elemental semiconductors, however.

In the theoretical description of these states it has been suggested that the electrically neutral isoelectronic substituent must first trap one electronic particle, whereupon a second particle of opposite type can become bound in the Coulomb field of the first to form the B.E. state.^{4,6} The first particle is bound to the impurity atom by short-range non-Coulombic forces. A bound state can occur only if these forces are sufficiently strong, otherwise the isoelectronic impurity merely acts as a scattering center.⁷ The scattering cross section of such a center may be relatively large for one type of electronic particle, however. If a bound state exists at all in a given situation, it seems to be possible to predict whether an electron or a hole will be bound at the isoelectronic trap simply from a consideration of the difference in the electronegativities of the impurity atom and the atom it replaces.⁸ Thus in GaP it is expected that N should be a neutral electron trap, whereas Bi should be a neutral hole trap. This expectation has been confirmed rather indirectly from the observed differences in the phonon-assisted transitions associated with the two B.E. states formed by j - j coupling between the electron and hole trapped at these two impurities.⁴

In the present paper, the first direct experimental evidence for the existence of a bound state for a single particle at an isoelectronic impurity is presented.⁹ New luminescence spectra have been observed from GaP crystals double-doped with Bi isoelectronic impurities and one of the group-VI donors S, Se, or Te. The properties of the new spectra are consistent with the radiative recombination of holes at the Bi isoelectronic traps with electrons at these *remote* donors.¹⁰ These transitions are examples of a new type of interimpurity (pair) electron-hole recombination process in which

⁶ R. A. Faulkner and J. J. Hopfield, in *Proceedings of the International Conference on Localized Excitations, Irvine, California* edited by R. F. Wallis (Plenum Press, Inc., New York, 1968), p. 218.

⁷ This is true, for example, when P is replaced by As in GaP.

⁸ It appears that bound states are produced in practice only for extreme differences in electronegativity. The magnitude of the binding energy is probably also sensitive to the lattice distortion produced by the impurity atom.

⁹ Transitions qualitatively similar to those discussed in this paper have been observed in GaP doped with O and Zn and with O and Cd; see C. H. Henry, P. J. Dean, and J. D. Cuthbert, *Phys. Rev.* **166**, 745 (1968). Here the electron is deeply trapped at O-Zn or O-Cd nearest-neighbor donor-acceptor pairs, however. These complexes may be regarded as two-component isoelectronic "molecular" substituents, to be distinguished from simple point defects like Bi substituents.

¹⁰ No evidence has been found in the present work for aggregation of the Bi-donor pairs. The Bi-donor pairs are similar in this respect to donor-acceptor pairs, where it has been observed that even if aggregation occurs on nearest-neighbor sites (e.g., as seen in Zn-O and Cd-O pair spectra), it is an insignificant effect when the substitutional impurities are both on the same sublattice, and the minimum possible pair separation is *second* nearest neighbor (e.g., C-O pair spectra). See P. J. Dean, C. H. Henry, and C. J. Frosch, *Phys. Rev.* **168**, 812 (1968).

the optical transition energy does not vary greatly with the pair separation (see Sec. III C, however). From the position of the relatively narrow no-phonon transition in these spectra, together with the independently known ionization energies of the group-VI donors, the hole binding energy of the Bi traps is measured to be ~ 40 meV.

II. EXPERIMENTAL

A. Crystal Preparation

Gallium phosphide crystals were grown from Ga solution at $\sim 1100^\circ\text{C}$ in sealed-fused silica capsules using techniques designed to reduce the concentrations of unwanted impurities, particularly C and N, to tolerable levels.¹¹ The crystals were doped with the desired impurities, S, Se, or Te donors and Bi isoelectronic traps, by the addition of the appropriate quantities of the metals or of Ga₂S to the Ga solution.

B. Measurement of Spectra

Luminescence spectra were recorded in the temperature interval 6.5– $\sim 30^\circ\text{K}$ under excitation by focused radiation from an HBO 200-W mercury arc lamp filtered by two Corning 7.59 glass filters. Combinations of calibrated wire gauze and Spectra Physics neutral density filters were sometimes used to regulate the excitation intensity in a known way. The temperature was adjusted by a stream of cold helium gas.¹² Optical transmission spectra were also recorded in the vicinity of the absorption lines due to the creation of excitons bound to the neutral shallow group-VI donors. The concentrations of the neutral donors were estimated from the strength of these no-phonon lines.¹³ Independent checks on these concentrations were also obtained from surface barrier capacitance estimates of $N_D - N_A$.¹⁴ The relatively heavily double-doped thin-plate crystals required for the observation of the Bi-donor pair luminescence contained many fizzes and inclusions. It was therefore not readily possible to obtain estimates of N_D and N_A from Hall-effect measurements.

Time-resolved luminescence spectra were measured after excitation by 100-nsec pulses of 300-keV electrons with the crystals immersed in liquid helium pumped below the λ point.¹⁵ The luminescence was passed through an f/6.8 scanning spectrometer and detected by a photomultiplier. An analog voltage from the vertical deflection amplifier of a sampling oscilloscope, triggered coincidentally with the excitation of the

¹¹ D. G. Thomas and R. T. Lynch, *J. Phys. Chem. Solids* **28**, 433 (1967).

¹² A simple Dewar was used of the type described by K. Maeda, *J. Phys. Chem. Solids* **26**, 595 (1965).

¹³ P. J. Dean, *Phys. Rev.* **157**, 655 (1967).

¹⁴ H. G. White and R. A. Logan, *J. Appl. Phys.* **34**, 1990 (1963).

¹⁵ The technique used has been described in more detail by J. D. Cuthbert and D. G. Thomas (Ref. 5); *Phys. Rev.* **154**, 763 (1967).

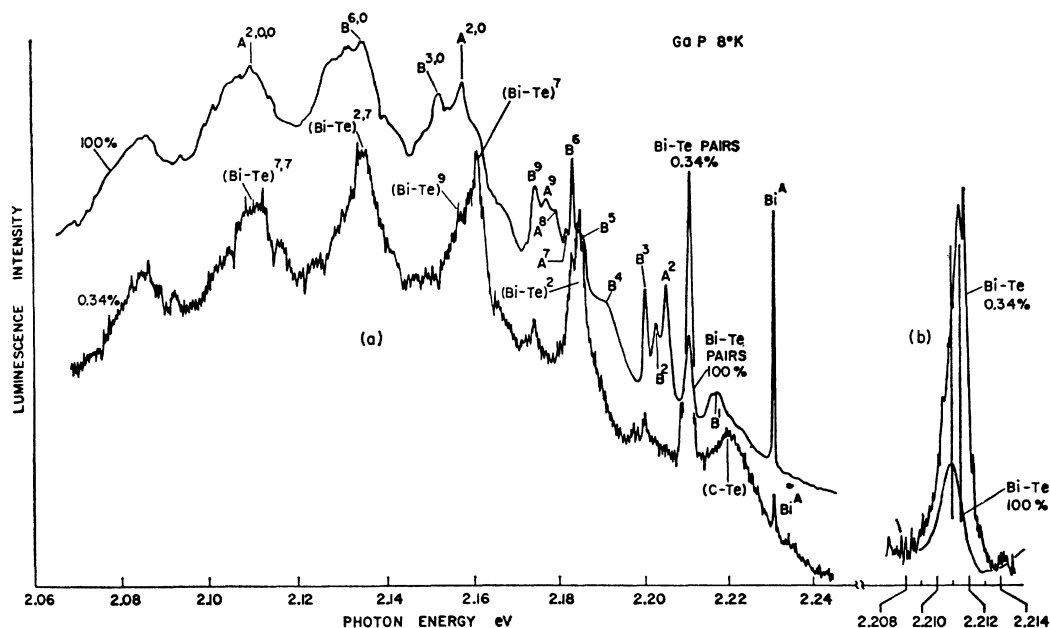


FIG. 1. (a) Comparison of low-temperature photoluminescence spectra from a GaP crystal containing $\sim 3 \times 10^{17} \text{ cm}^{-3}$ Bi and $\sim 1.5 \times 10^{18} \text{ cm}^{-3}$ neutral Te donors at two levels of excitation intensity differing by a factor of ~ 300 . The no-phonon lines of the Bi B.E. and Bi-Te pair spectra, respectively, appear near 2.23 and 2.21 eV. Other structure is due to Stokes phonon-assisted recombinations (see Table II). Note that the pair and B.E. spectra are favored at low- and high-excitation intensities, respectively. (b) No-phonon Bi-Te pair photoluminescence bands compared at the two excitation levels used in (a). Note the small shift of the peak to lower energy caused by the increase in the excitation intensity.

crystal, was proportional to the applied photomultiplier response within a time interval defined by the setting of the oscilloscope sampling window. This signal was fed to the Y axis of an X - Y recorder. The wavelength analog voltage from the spectrometer was fed to the X axis. Luminescence decay curves were obtained with a similar arrangement, except that the spectrometer was set at a fixed wavelength and the X deflection of the recorder was governed by the time analog voltage from the oscilloscope. The spectral resolution in these time resolved measurements was $\sim 0.5 \text{ meV}$, somewhat larger than in the dc spectra (typically ~ 0.2 to $\sim 0.3 \text{ meV}$).

III. RESULTS AND DISCUSSION

A. dc Excited Luminescence Spectra

The first evidence of the new type of radiative pair transition was obtained during studies of the quenching effect of high concentrations of neutral S donors on the efficiency of radiative recombinations at Bi isoelectronic traps in GaP.¹⁶ A spectrum containing a rather broad no-phonon line, $\sim 35 \text{ meV}$ below the Bi B.E. A line, and prominent broad phonon replicas at still lower transition energies, was observed in luminescence spectra recorded at $\sim 20^\circ\text{K}$ from many crystals doped with $\sim 10^{18} \text{ cm}^{-3}$ neutral S donors. The new spectrum was usually hard to distinguish from the Bi B.E.

luminescence spectrum and the luminescence spectrum due to electron-hole recombinations at remote pairs of sulphur donors and inadvertently present carbon acceptors¹⁷ (C-S pair spectrum).

Further investigation showed that the new transitions are most prominent relative to the B.E. luminescence in spectra recorded at the lowest possible excitation intensities (Sec. III C) and at very low temperatures (Sec. III D). For example, in a Bi, Te-doped crystal below $\sim 15^\circ\text{K}$, the B.E. spectrum was predominant at the highest available excitation intensities, whereas the new spectrum was predominant at the lowest usable excitation intensity [Fig. 1(a)]. Since Bi is believed to be a trap for photoexcited free holes in GaP, it is plausible to suggest that the new spectrum is caused by radiative recombinations of these holes with electrons trapped at remote Te donors (Bi-Te pairs). Transitions at remote pairs have low oscillator strength, so that the typical saturation behavior of the new luminescence relative to the B.E. luminescence, shown in Fig. 1, is readily understandable.

Proof that shallow donors are involved in the new radiative transitions was afforded by a comparison of luminescence spectra obtained from Bi-doped crystals

¹⁶ J. C. Tsang, P. J. Dean, and P. T. Landsberg, *Phys. Rev.* **173**, 814 (1968).

¹⁷ Carbon, not Si, is the shallow acceptor in the residual shallow donor-acceptor pair luminescence spectrum usually prominent in solution-grown GaP which has not been deliberately doped. P. J. Dean, C. J. Frosch, and C. H. Henry, *J. Appl. Phys.* **39**, 5631 (1968). This work confirms that Si is a deep acceptor in GaP as originally suggested by M. Lorenz and M. H. Pilkuhn, *J. Appl. Phys.* **38**, 61 (1967).

containing three different group-VI donor impurities. Figure 2 shows that the no-phonon transition energy of the new spectrum varies with the donor. These differences in the transition energies (Table I) are equal to the differences in the donor ionization energies, which are accurately known from analyses of shallow donor-acceptor pair spectra¹⁸ and also from radiative "two-electron" recombination spectra of excitons bound to isolated group-VI donors.^{19,20} The assumption that Bi is involved in these spectra is proved by the fact that the new spectra have only been observed from GaP crystals containing appreciable concentrations of Bi, which is not an inadvertent impurity in GaP.

These new pair spectra differ qualitatively from the shallow donor-acceptor pair spectra since, unlike a group-II acceptor, the Bi hole trap is neutral before hole capture. Ignoring polarization effects (Sec. III C), the no-phonon recombination energy $h\nu$ of a hole and electron bound to a remote Bi-donor pair is then simply given by

$$h\nu = E_g - (E_h + E_D), \quad (1)$$

where E_g is the energy gap and E_h and E_D are, respectively, the binding energies of holes at the Bi isoelectronic traps and electrons at shallow donors.

Table I shows that E_h is ~ 40 meV independent of the donor if $h\nu$ is measured at the peaks of the no-phonon lines in the new pair spectra recorded at low excitation intensities. According to the position of the A no-phonon line in the B.E. luminescence spectrum, which represents the decay of bound excitons from the $J=1$ state,²¹ the total binding energy of the electron and hole at the Bi isoelectronic trap is ~ 107 meV. The binding energy of the electron to the hole is not simply

TABLE I. Analysis of no-phonon transition energies in the Bi-donor pair spectra.

Donor	$h\nu_{\text{peak}}$ eV ^a	$(E_h + E_D)$ meV ^b	E_h meV ^c
S	2.1968 ± 0.0003	141.7 ± 1	39.7 ± 1
Se	2.1979 ± 0.0002	140.6 ± 1	39.7 ± 1
Te	2.2114 ± 0.0002	127.1 ± 1	39.6 ± 1

^a Absolute errors are quoted. Relative values of $h\nu_{\text{peak}}$ are accurate to ± 0.1 meV for Se and Te and ± 0.2 meV for S and Se or S and Te.

^b The major error in the absolute values of $E_h + E_D$ calculated from $h\nu_{\text{peak}}$ according to Eq. (1) is the uncertainty in E_g , here taken to be 2.3385 ± 0.001 eV. Differences between $E_h + E_D$ for the different donors are accurate to $\sim \pm 0.2$ meV.

^c Differences accurate to ± 0.2 meV. Calculated assuming $(E_D)_S = 102 \pm 0.5$ meV (Ref. 20) and $(E_D)_S - (E_D)_{Se} = 1.7 \pm 0.1$ meV, $(E_D)_S - (E_D)_{Te} = 14.5 \pm 0.2$ meV.

¹⁸ F. A. Trumbore and D. G. Thomas, Phys. Rev. **137**, A1030 (1965).

¹⁹ P. J. Dean, J. D. Cuthbert, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters **18**, 122 (1967). R. A. Faulkner (private communication) has recently shown that s -like rather than p -like donor excited states are involved in these "two-electron" spectra and has obtained the new values of E_D discussed in Ref. 17 from a reanalysis of these spectra.

²⁰ Recently revised values for the ionization energies of shallow donors and acceptors in GaP are discussed in Ref. 17.

²¹ The spins of the electron and hole are antiparallel in this state, and the B.E. transition is allowed (see Ref. 2).

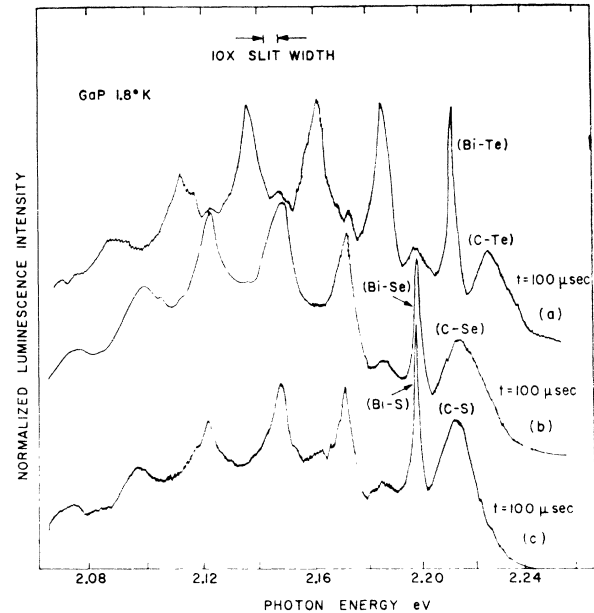


Fig. 2. Low-temperature time-resolved cathodo-luminescence spectra from three GaP crystals doped with Bi and separately with Te, Se, and S donors at concentrations $\sim 10^{18}$ cm⁻³. For the time delay of 100 μ sec shown only the Bi-donor and C-donor pair spectra are significant. The indicated no-phonon lines of both of these types of pair spectra are mutually displaced according to the difference in ionization energies of the group-IV donors in GaP (Table I). Note the marked difference in breadth of the C-donor and Bi-donor no-phonon pair lines.

equal to the difference between these two energies, however, because electron-hole correlation effects are very important when the binding energies of the two particles are comparable, as they evidently are here.²² When the electron is trapped by the hole at the Bi atom, the electron can gain Coulomb interaction energy if the hole wave function is compressed. This gain in interaction energy is eventually balanced by the increase in the KE of the hole. Correlation effects are extremely difficult to calculate when they represent a large fraction of the total binding energy, as is likely in the present instance.²³

B. Time-Resolved Spectra

The Bi-donor pair recombination spectra were most readily separated from the overlapping Bi B.E. spectrum in time-resolved measurements as is shown in Fig. 3 for Bi-Te pair transitions. The spectrum recorded during excitation by the pulsed electron beam ($t=0$) is identical to that observed in crystals doped with Bi alone. It is predominantly due to phonon-assisted recombinations from the B ($J=2$) state of the B.E., although the no-phonon transition from the A state

²² These correlation effects were legitimately ignored in Ref. 9, since the ionization energy of the electron is ~ 10 times larger than the ionization energy of the hole for the O-Zn or O-Cd B.E. states.

²³ We are indebted to R. A. Faulkner for several enlightening discussions of this matter.

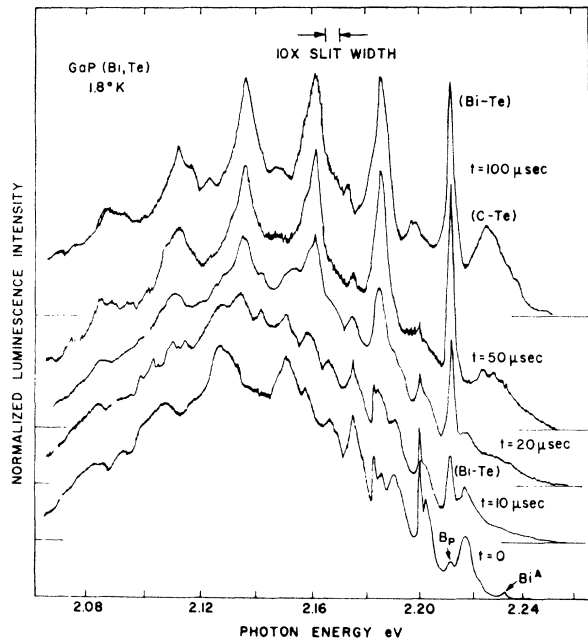


FIG. 3. Low-temperature time-resolved cathodo-luminescence spectra from a Bi,Te-doped GaP crystal showing the decreasing contribution of the Bi B.E. spectrum and the increasing contribution from the Bi-Te pair spectrum with increase in the delay time. The greater complexity of the vibronic structure in the B.E. spectrum is evident [see Fig. 1(a) and Table II].

appears weakly. As the delay between the excitation pulse and the setting of the oscilloscope sampling window is increased from zero, the Bi-Te pair band appears and becomes predominant for delay times $\gtrsim 20 \mu\text{sec}$ under the experimental conditions used in Fig. 3.²⁴ Consistent with Fig. 1, it was found that the relative proportions of these two transitions in the time-resolved spectra varied with the excitation intensity produced by the electron pulses, the pair transitions being most prominent at the lower excitation intensities.

Although the crystals used in these measurements were deliberately doped only with Bi and one of the group-VI donors, shallow C acceptors were also inadvertently present. Pair transitions involving holes bound to these acceptors were also present in the delayed time-resolved spectra (Figs. 2 and 3). It was not possible to separate the C-donor and Bi-donor pair spectra by time-resolved spectroscopy, so the intensity decay rates of these two recombination processes are very similar. The Bi-donor pair luminescence exhibits the nonexponential power-law type of time decay (Fig. 4) which has been extensively studied for shallow donor-acceptor pair recombinations

²⁴ It should be particularly noted in comparing the $t=0$ and the delayed spectra in Fig. 3 that the component B_p is an $\sim 18\text{-meV}$ phonon replica of the B bound exciton transition. It is *not* a weak contribution from the no-phonon line of the Bi-Te pair spectra, which is prominent in the delayed spectra, although it falls at very nearly the same energy.

in GaP.²⁵ Figure 4 also shows the relatively fast decay of the Bi B.E. luminescence measured in the same crystals under the same excitation conditions as the Bi-donor pair luminescence. The decay of the B.E. luminescence in these crystals at low temperatures was very similar to that previously measured from crystals in which Bi was the only intentionally added impurity.²⁶ This B.E. decay is accurately exponential, with a temperature-independent decay time below $\sim 5^\circ\text{K}$ characteristic of the B exciton state.

C. Shift in the Bi-Donor Pair Spectrum with Excitation Intensity

It is evident from Fig. 1(b) that the no-phonon line of the Bi-Te spectrum is asymmetrical, with a broader tail on the *low*-energy side. This can be seen most clearly at low excitation intensities, when the Bi bound exciton luminescence is relatively weak. In addition the peak energy shifts $\sim 0.6 \text{ meV}$ to *lower* energy for a 300-fold increase in the excitation intensity.²⁷ This shift is opposite in direction and much smaller than that produced under similar conditions in a donor-acceptor pair spectrum in GaP ($\sim 10 \text{ meV}$). The donor-acceptor pair spectra are also asymmetrical, even at low-excitation intensities, but in this case the broader wing is on the *high*-energy side (Fig. 5).

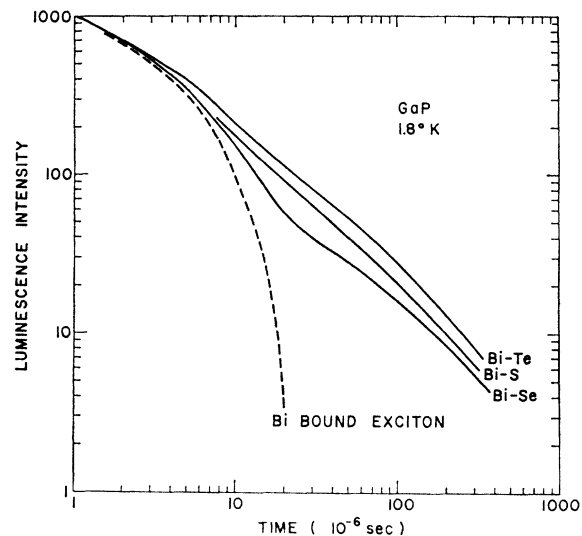


FIG. 4. Time decay of the intensity of the low-temperature cathodo-luminescence in the no-phonon lines of the Bi B.E., and the Bi-donor pair spectra in GaP. The decay of the bound exciton luminescence is short and exponential, in contrast to the pair spectra.

²⁵ D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. **140**, A202 (1965).

²⁶ J. D. Cuthbert and D. G. Thomas, Phys. Rev. **154**, 763 (1967).

²⁷ This shift was not caused by an increase in crystal temperature, since the energy of the Bi B.E. A line remained constant (to within $\pm 0.1 \text{ meV}$) under the 300-fold increase of excitation intensity.

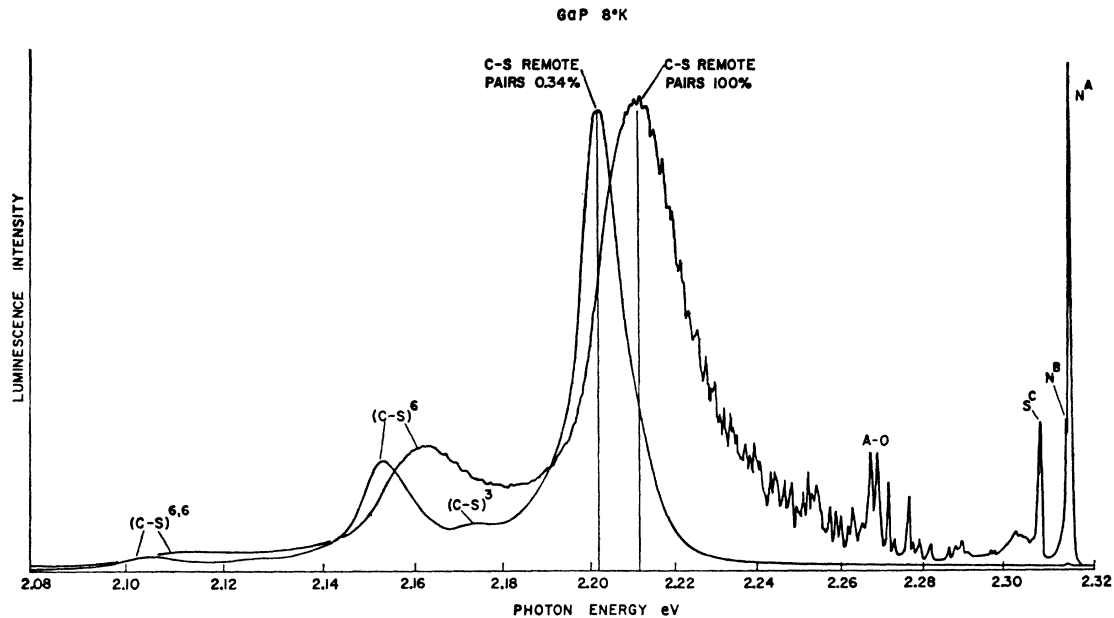


FIG. 5. C-S acceptor-donor pair spectrum recorded from a GaP crystal at the two levels of photoexcitation used in Fig. 1. Note that the shift in the peak energy produced by the change in excitation intensity is much larger than in the Bi-Te pair spectrum shown in Fig. 1(b), and is in the opposite direction. Sharp luminescence lines due to the decay of excitons bound to N isoelectronic substituents and to neutral S donors are prominent in the luminescence spectrum recorded at high-excitation intensity.

The shift in the donor-acceptor pair spectrum arises because transitions at remote pairs, which have low oscillator strength, saturate with increasing excitation intensity relative to those at close pairs. The transition energy for the close pairs is greater than for the more remote pairs because of an additional term on the right-hand side of Eq. (1), which accounts for the electrostatic interaction between the charges at the ionized donor and acceptor centers.²⁸ For sufficiently large values of the pair separation r , in practice for $r \gtrsim 20 \text{ \AA}$ for shallow C-S pairs in GaP,¹⁷ this term is simply $+e^2/\epsilon r$, where e is the electronic charge and ϵ is the low-frequency dielectric constant.

As mentioned in Sec. III A, the large first-order Coulomb interaction term does not appear in the transition energy of the Bi-donor pairs because the Bi trap is neutral before the hole is captured. The Bi-donor no-phonon line is therefore narrow compared with the C-S pair spectrum, even though transitions at pairs of widely varying separation contribute to both spectra, as indicated by the similarity in the decay rates (Fig. 4). The half-height bandwidths of the Bi-Te and C-S no-phonon bands in Figs. 1 and 3 are ~ 1.3 and ~ 12 meV, respectively, at low-excitation intensities. At high-excitation intensity both lines are broader; the Bi-Te spectral width is ~ 1.65 meV and the C-S spectral width ~ 24 meV. The Bi-Te no-phonon pair line is much broader than the Bi B.E. A line, which had a half-height bandwidth of ~ 0.23

meV for the crystal used in Fig. 1. Since the spectral line due to the no-phonon recombination of a hole and electron at a given Bi-Te pair should be even narrower than the B.E. A line,²⁹ it is natural to suppose that the broad asymmetrical shape of the Bi-Te band reflects the intensity distribution of transitions at pairs with different values of r , that is, there is a small shift in the transition energy with change in r .³⁰ This shift is far too small for transitions involving pairs with adjacent values of r to be resolved as discrete lines, in contrast to donor-acceptor pair spectra. The sense of the asymmetry and of the shift of the peak transition energy with change in the excitation intensity both suggest that the transition energy in the Bi-donor pair spectra *decreases* slightly with decreasing r , in contrast to the donor-acceptor pair spectra.

A plausible source of the dependence of the Bi-donor pair transition energy on the pair separation is the electrostatic polarization interaction between the two centers. This is likely to be predominant in the excited state of the electronic transition, where the binding energy of the electron to the donor core can be in-

²⁹ This is so because the Bi A line is broadened by spontaneous phonon emission to the B state, an effect which has been investigated for O isoelectronic substituents in ZnTe by R. E. Dietz, D. G. Thomas, and J. J. Hopfield, Phys. Rev. Letters 8, 391 (1962). This process cannot occur in the Bi-donor pair spectra.

³⁰ A shift of the order observed in the Bi-Te pair spectrum, $\lesssim 1$ meV, was too small to be detected in the qualitatively similar pair spectra observed in Zn (or Cd)-O doped GaP (Ref. 9) because the no-phonon pair transitions were not resolved and the phonon-assisted transitions were contained in a featureless band ~ 135 meV wide.

²⁸ D. G. Thomas, M. Gershenson, and F. A. Trumbore, Phys. Rev. 133, A269 (1964).

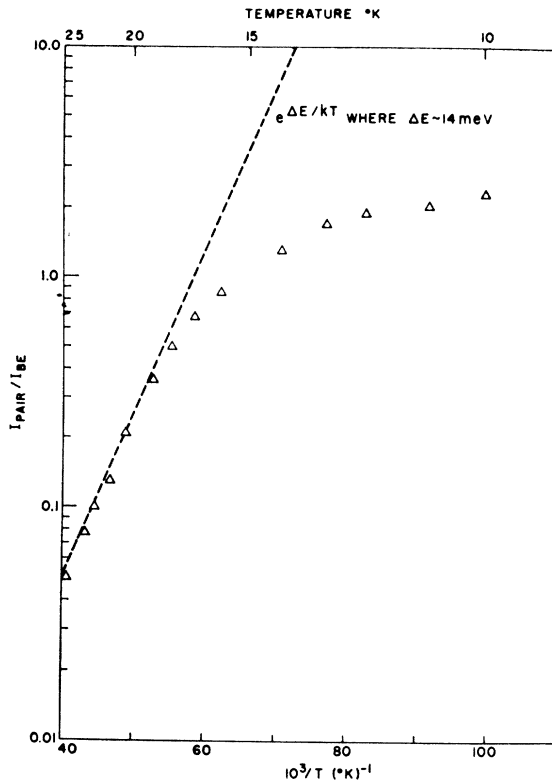


FIG. 6. Temperature dependence of the ratio of the intensities in the Bi-Te pair and the Bi B.E. photoluminescence spectra. The activation energy deduced above $\sim 18^\circ\text{K}$ is attributed to phonon-assisted electron tunneling between the Te donor level and the shallower Bi isoelectronic "donor" level.

creased by interaction with the positive hole trapped at the neutral Bi impurity.³¹ For a pair separation larger than the combined radii of the trapped electron and hole states, the hole can be treated as a point charge, and the interaction energy is

$$E_p = -\frac{9}{4} \frac{e^2}{\epsilon a} \left(\frac{a}{r}\right)^4, \quad (2)$$

where a is the ground-state radius of the donor.

If the donor ionization energy is increased by E_p , then the transition energy will decrease by a like amount according to Eq. (1). The magnitude of the spectral energy shift due to the change of pair separation for the modal pair transition with increasing excitation intensity can be roughly calculated from Eq. (2). It is assumed that these modal values of r are the same in the Bi-Te pair spectrum as they are in the C-S acceptor-donor pair spectrum recorded under similar conditions.³² The modal C-S transition energies

³¹ We assume here that the polarization of the neutral Bi atom by the positively charged ionized Te donor is negligible. The authors are indebted to R. A. Faulkner for suggesting this model.

³² Wave-function overlap is predominantly due to the trapped hole in both types of pair spectra, and E_h for the Bi hole trap is comparable with E_A for the C acceptor (~ 48 meV according to Ref. 17).

in Fig. 3 are 2.2019 and 2.2115 eV at the two different excitation levels, so that the respective values of $e^2/\epsilon r$ are ~ 13 and ~ 23 meV,³³ and $r_1 \sim 100 \text{ \AA}$, $r_2 \sim 55 \text{ \AA}$. With these values of r , and $a = 13 \text{ \AA}$ for Te donors in GaP, $\Delta E_p \sim 0.6$ meV according to Eq. (2). This calculated shift is identical with the shift observed in Fig. 1, as near as can be estimated. The agreement is evidently fortuitously good, particularly in view of the use of parameters from the C-S spectrum in the calculation of properties of the Bi-Te spectrum. The important point is that the calculation based on the assumed polarization interaction is consistent with both the *sign* and *magnitude* of the observed shift of the Bi-Te peak energy.

Equations (1) and (2) suggest that the shift of the modal Bi-donor transition energy should accelerate rapidly with increasing excitation intensity. In agreement with this prediction, it was observed that most of the measured spectral shift in the Bi-Te peak occurred near the high-intensity limit of the range used for Fig. 1(a). It was not possible to check this shift rate precisely over a range of different excitation intensities, however. The position of the Bi-Te no-phonon pair peak could not be accurately measured at significantly higher intensities than used in Fig. 1, where considerably larger shifts are predicted from Eq. (2), because the pair luminescence could then no longer be distinguished from the strong Bi B.E. luminescence.

D. Electron Tunneling between the Shallow Donor and Bi Impurity Atoms

The intensity of the Bi-donor pair luminescence decreases very rapidly relative to the Bi B.E. luminescence with increasing temperature in the range ~ 10 – 25°K . Figure 6 shows that this decrease in relative intensity is approximately exponential for the Bi-Te pair bond in the high-energy portion of this temperature range, with an activation energy of 14 ± 2 meV. The probability of thermal release of the electrons and holes trapped at the Te donors and Bi atoms is small in this temperature range compared with the radiative recombination probability.¹⁶ The rapid quenching of the Bi-donor pair luminescence is believed to be due to the phonon-assisted tunneling of electrons from the donors to nearby Bi atoms which have already trapped a hole (the ionized Bi "donor" in the sense of Ref. 4).

The time-resolved spectra shown in Fig. 7 can be readily interpreted on the phonon-assisted tunneling model. The prompt spectrum at 4.2°K is due to Bi B.E. recombinations, whereas after a 20 - μsec delay the luminescence is predominantly due to hole-electron recombinations at Bi-donor pairs, as discussed in Sec. III B and illustrated in Fig. 3. At 13°K , near the

³³ A recently recalculated value of the transition energy for a pair of infinite separation has been used to obtain these values of $e^2/\epsilon r$ (see Ref. 17).

onset of thermal quenching of the Bi-donor pair luminescence, the prompt and delayed spectra remain distinct. A dramatic change occurs above 13°K, however. Figure 7 shows that the delayed spectrum has become indistinguishable from the prompt Bi B.E. spectrum by 25.5°K. This indicates that electron tunneling between the Te donor and the filled Bi hole trap is a much more rapid process than the radiative recombination channel for a typical Bi-donor pair at this temperature. The excitation is transferred to the

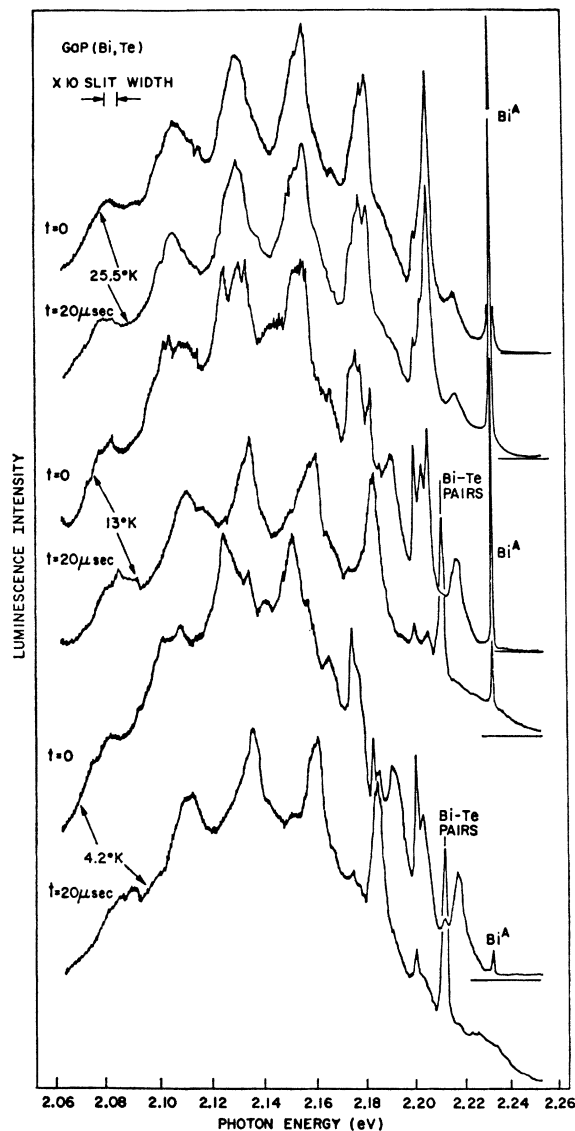


FIG. 7. Prompt and delayed time-resolved cathodo-luminescence spectra from a Bi,Te-doped GaP crystal at three temperatures. The prompt spectrum is due to Bi B.E. recombinations, whereas after 20- μ sec delay the luminescence is almost entirely due to Bi-Te pair recombinations at 13°K as well as at 4.2°K (see Fig. 3). The prompt and delayed spectra are indistinguishable at 25.5°K. At this temperature the Bi-Te pair recombinations are quenched by the transfer of electrons from the Te to the Bi impurities through phonon-assisted tunneling.

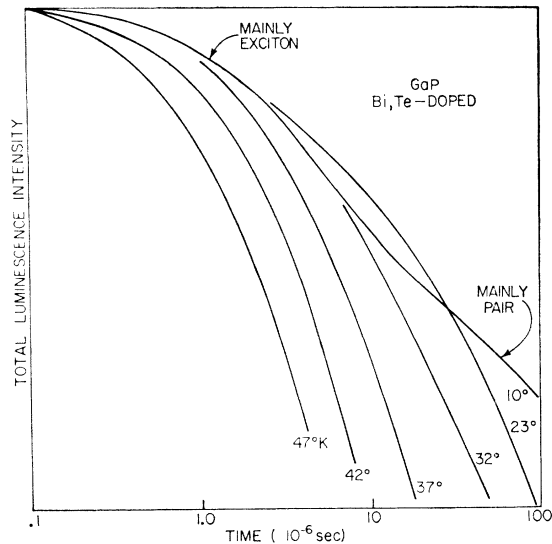


FIG. 8. Time decay of the spectrally integrated intensity of cathodo-luminescence due to Bi B.E. and Bi-Te pair recombinations in GaP at various temperatures. Contributions to the decay arising from these two recombination processes can be distinguished through their decay rates at 10°K or below but not above 23°K because of phonon-assisted tunneling of electrons between the Te and Bi impurities. This tunneling process greatly reduces the luminescence intensity at long delay times at the higher temperatures. Above \sim 30°K the decay becomes exponential and similar to the decay of Bi B.E. luminescence observed in GaP crystals in which Bi is the only intentionally added impurity. The decay time is shortened by thermal dissociation of the B.E. state in this temperature range.

fast radiative Bi B.E. state by the phonon-assisted tunneling mechanism within Bi-donor pairs which would have decayed radiatively in a time long compared with 20 μ sec. The fast time decay of the Bi B.E. transition is slightly *lengthened* between 10 and 23°K (Fig. 8) as the result of tunneling transitions from the Bi-donor pair states. A further important feature of Fig. 8 is the large reduction in the relative intensity of the long-lived luminescence observed above 10°K, which is also attributed to tunneling. The net effect is that it is impossible to distinguish in the time decay the individual contributions due to Bi B.E. and Bi-donor pair transitions at temperatures where the tunneling mechanism is operative.

Interimpurity tunneling is a probable process at the donor concentrations used in these experiments ($\sim 10^{18}$ cm $^{-3}$), which are not far below the threshold for donor impurity banding ($\sim 5 \times 10^{18}$ cm $^{-3}$ according to Ref. 16). Evidence of hole tunneling from shallow Zn acceptors was recently observed at similar impurity concentrations through its effect on the relative intensities of the red B.E. and pair bands associated with Zn-O nearest-neighbor pairs in GaP.³⁴

In the present instance, if the Bi B.E. radiative decay rate is large compared with the rate at which

³⁴ J. D. Cuthbert, C. H. Henry, and P. J. Dean, Phys. Rev. 170, 739 (1968).

TABLE II. Comparison of phonon energies associated with the principal replicas in various spectra involving shallow donors, acceptors, and Bi traps on P sites in GaP.

Bi bound exciton		Bi-donor pair		Donor-acceptor pair	
Component	Phonon energy (meV)	Component	Phonon energy (meV)	Component	Phonon energy (meV)
B^1	11.9± 0.3				
A^2	26.2± 0.2	(Bi-Te) ²	26.4± 0.3		
B^2	25.9± 0.2				
B^3	28.5± 0.2			(C-S) ³	28.5± 0.5
B^4	37.8± 0.3				
B^5	43.0± 0.3				
B^6	45.7± 0.2				
A^7	50.0± 0.2	(Bi-Te) ⁷	49.9± 0.2	(C-S) ⁷	49.5± 0.5
A^8	52.0± 0.3				
A^9	54.6± 0.3	(Bi-Te) ⁹	54.2± 0.4		
B^8	54.5± 0.2				
$A^{2,0}$	26.2+48.6	(Bi-Te) ^{2,7}	26.4+49.7		
$B^{3,0}$	28.5+48.6				
$B^{6,0}$	45.7+48.8				
$A^{2,0,0}$	26.2+48.6+49	(Bi-Te) ^{7,7}	~50 +50	(C-S) ^{7,7}	49.5+50

electrons can tunnel from the neutral Te donors,³⁵ the intensity ratio of Bi-Te pair and Bi B.E. luminescence bands is

$$I_{\text{pair}}/I_{\text{B.E.}} = 1/(A + W_T/W_{\text{pair}}), \quad (3)$$

where A depends upon the Bi B.E. transition probability, on the excitation intensity, on the donor concentration, and on the average transition probability for the Bi-Te pairs. The ratio W_T/W_{pair} of the phonon-assisted tunneling probability and the radiative recombination probability of an electron and hole for a given Bi-Te pair of separation r is given by³⁶

$$\frac{W_T}{W_{\text{pair}}} = \frac{V^2 e^{-\hbar\omega/kT} W_{\text{max}} e^{-2r/a}}{W_{\text{max}} e^{-2r/a}} = V^2 e^{-\hbar\omega/kT}, \quad (4)$$

where V is the interaction potential which mixes the electron states at the Te and Bi donors, $\hbar\omega$ is the energy of the phonon required for the nonhorizontal one-phonon-assisted electron tunneling between these states,³⁷ a is the Bohr radius of the electron or hole

³⁵ Te-Bi tunneling, like Bi B.E. recombinations (Fig. 1) is a second-order process involving phonon cooperation. The relative rates of these transitions will be mainly determined by the wavefunction overlap of the relevant electronic particles. The measurements used in Fig. 6 were obtained from spectra recorded at low excitation intensities, where the Bi-Te pair separation at the peak of the no-phonon band is ~ 100 Å (Sec. III C). The maximum radius of the ground-state electron wave function of the Te donor is given by $a = \hbar/(2m_t^* E_D)^{1/2}$, where m_t is the transverse electron mass, ~ 0.26 times the free electron mass. Thus a is ~ 13 Å (Sec. III C). The binding energy of the electron in the Bi B.E. complex is not known precisely, but must be of order $\frac{1}{2}(E_D)_{\text{Te}}$, i.e., ~ 45 meV. Thus the radius of the electron wave function in this complex is ~ 18 Å. The typical Bi-Te pair separation relevant to this analysis is therefore approximately 3 times the combined radii of the electron bound states at the two sites, whereas the electron and hole wave functions in the Bi B.E. are of comparable extent and overlap completely.

³⁶ The authors are grateful to C. H. Henry for helpful discussions concerning Eq. (4).

³⁷ The phonon occupation number has been simplified in this expression, since $\hbar\omega \gg kT$.

bound to the Bi impurity,³⁸ W_{max} is the pair transition rate for maximum overlap of the electron and hole wave functions (i.e., when $r=0$), and k is Boltzmann's constant. Combining Eqs. (3) and (4), the temperature dependence of the intensity ratio $I_{\text{pair}}/I_{\text{B.E.}}$ is essentially given by

$$I_{\text{pair}}/I_{\text{B.E.}} = 1/(A + B e^{-\hbar\omega/kT}), \quad (5)$$

where both A and B are relatively independent of temperature in the low-temperature range illustrated in Fig. 6. The exponent ΔE in Fig. 6³⁹ can therefore be identified with $\hbar\omega$, which is expected to be just the energy separation δE between the Bi-Te pair and the Bi B.E. no-phonon lines (20 meV according to Table I). The activation energy ΔE measured near the high-temperature limit of Fig. 6 is in fact significantly less than this energy separation. This is perhaps not surprising since the thermal ionization energies of shallow donors in GaP crystals containing $\sim 10^{18}$ cm⁻³ neutral donors, like the crystal used here, are appreciably reduced⁴⁰ because of incipient impurity banding.¹⁶ In view of this, the relationship between the observed values of ΔE and δE is taken as reasonable evidence for the validity of the tunneling model for the tem-

³⁸ Since the ionization energy of the Te donor is probably about twice that of the Bi isoelectronic "donor," the tunneling rate is mainly determined by the spread of the electron wave function in the latter state. For a similar reason, the pair transition rate is mainly determined by the extent of the wave function of the hole trapped at the Bi atom. The radii of these two diffuse states are believed to be comparable, and for simplicity they have been made equal in Eq. (4) (see Refs. 25 and 35).

³⁹ Equation (5) is approximated at high temperatures (above $\sim 19^\circ\text{K}$) by the simple exponential form used in Fig. 6. Data obtained using penetrating electron excitation with a low-intensity dc beam conformed to Eq. (5) down to $\sim 14^\circ\text{K}$, with $\hbar\omega \sim 14$ meV and using a value of A determined at 4°K . Little change in the intensity ratio $I_{\text{pair}}/I_{\text{B.E.}}$ occurred between 4 and 14°K , particularly at low-excitation intensity.

⁴⁰ H. C. Montgomery and W. H. Feldman, J. Appl. Phys. 36, 3228 (1965) and H. C. Montgomery (private communication).

perature-dependent intensity ratio of the Bi-donor pair and Bi B.E. luminescence bands.

E. Phonon Selection in the Bi Bound Exciton and Bi-Donor Pair Spectra

The energies of the principal components in the vibronic structure in the Bi luminescence spectra are compared in Table II and the relative strengths of these components are shown in Fig. 1. The prominent replicas in the Bi-donor pair spectra are much more like those associated with the Bi B.E. *A* state rather than with the *B* state. This is not surprising, since the vibronic structure in the Bi B.E. *B*-state spectrum, best observed at 1.6°K ($t=0$ spectrum in Fig. 3), mainly involves phonons of symmetry which can mix the *A* and *B* states of the bound exciton.⁴ These states cannot be investigated separately in the Bi-donor pair spectra, since the spin-spin interaction energy between an electron and hole bound to a remote pair is negligibly small. The phonon structure in the Bi B.E. and Bi-donor pair spectra should exhibit considerable similarities if the phonon coupling is mainly associated with the short-range interaction between the hole and the neutral Bi trap, as is believed to be the case. Differences can arise, however, if the wave function of the hole is appreciably distorted by the influence of the electron which it traps to make the B.E. state.⁴¹ Comparison of the $t=0$ and $t=100$ - μ sec spectra in Fig. 3 shows that this effect produces noticeable changes in the details of the vibronic structure but not in the over-all strength of the hole-phonon interaction.

The energies of phonons resolved in the shallow C-S donor-acceptor pair spectrum are also listed in Table II for comparison with the Bi spectra. Since the C and Bi hole traps are on the same (*P*) lattice site, this comparison is unaffected by the selection rules for indirect phonon-assisted transitions recently discussed by Morgan.⁴²

IV. SUMMARY

Electrons bound to shallow donors can recombine radiatively with holes bound to Bi isoelectronic traps in GaP. This recombination process is most easily seen when the donor concentration exceeds the Bi concentration and when both concentrations are as large as possible within the limits imposed by the formation of a donor impurity band. The Bi-donor pair lumi-

nescence spectra are superficially similar to the 20°K Bi B.E. spectrum, although only one no-phonon line is resolved in the pair spectra even at the lowest temperatures. The Bi-donor pair no-phonon line is broad compared with each of the Bi B.E. no-phonon lines, but is appreciably narrower than the no-phonon bands previously reported for unresolved shallow donor-acceptor pair recombinations in GaP. Like the donor-acceptor pair spectra, the breadth of the Bi-donor pair no-phonon line is mainly due to the presence of many unresolved transitions at pairs of different separation. The sense of the spectral asymmetries and of the energy shifts of these pair spectra under changes in the excitation intensity indicates that the Bi-donor pair transition energy *decreases* with decreasing pair separation, opposite to the dependence observed for the donor-acceptor pair transition energy. The magnitude and direction of this dependence of the Bi-donor pair transition energy on pair separation can be accounted for by the electrostatic polarization interaction between the hole bound at the Bi isoelectronic trap and the neutral donor. The transition energies in the Bi-donor pair spectra do not contain the much larger first-order Coulomb interaction term, characteristic of the donor-acceptor pair spectra, because the Bi hole trap is neutral before the hole is trapped.

The Bi-donor spectra cannot provide information about the types of lattice site occupied by these impurities, unlike the donor-acceptor pair spectra, since the energy shifts due to the polarization interaction are too small to enable transitions at individual pairs to be resolved. The *existence* of the Bi-donor luminescence spectra confirms the theoretical prediction that an isoelectronic substituent like Bi can trap a single electronic particle (hole), however. The binding energy of the hole can be simply obtained from the no-phonon transition energies of the Bi-donor pair spectra.

The time decay of the Bi-donor pair luminescence is slow and nonexponential because pairs of variable, large separation are involved. Phonon-assisted electron tunneling between the group-IV donors and the Bi "donor" occurs with increase in temperature above $\sim 13^\circ\text{K}$. The relatively fast Bi B.E. transition becomes completely predominant above $\sim 25^\circ\text{K}$ for the crystals used in the experiments reported in the present paper. The intensity ratio of the Bi-donor pair and the Bi B.E. luminescence decreases exponentially with increase in temperature above the threshold at $\sim 13^\circ\text{K}$, as anticipated. The measured activation energy is significantly less than the difference between the Bi-exciton and Bi-Te pair transition energies, however. Better agreement between these parameters might be found at lower impurity concentrations.

⁴¹ This difference was found to be negligible for the red luminescence characteristic of Zn (or Cd)-O doped GaP (see Ref. 22).

⁴² T. N. Morgan, Phys. Rev. Letters **21**, 819 (1968).