Concentration Quenching of Luminescence by Donors or Acceptors in Gallium Phosphide and the Impurity-Band Auger Model

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The low-temperature photoluminescence efficiency for near band-gap transitions in GaP is shown to be a rapidly decreasing function of the donor or acceptor concentration above a well-defined threshold impurity concentration near 10^{18} cm^{-3}. The concentration quenching is nearly temperature-independent below $\sim$40°K and is insensitive to the nature of the luminescence center. The threshold impurity concentration for concentration quenching lies close to the threshold predicted for intermediate-type impurity-band conduction involving shallow donors and acceptors in GaP. The luminescence quenching is attributed to radiationless Auger recombinations in which the recombination energy of the luminescence center is entirely given up to delocalized impurity electrons (or holes) in the impurity band. These free carriers are ejected deep into the electronic energy bands of GaP, and the high kinetic energy of these carriers is subsequently lost in cascade phonon-emission processes. This impurity-band Auger model for the radiationless recombination predicts the experimentally observed sharp increase in quenching above 10^{18} cm^{-3} which cannot be accounted for on the alternative hypothesis of capture competition between independent luminescent and nonradiative centers. The model is also consistent with the absence of concentration quenching at high concentrations, $\gtrsim 10^{19}$ cm^{-3}, of isoelectronic impurities in GaP. The temperature dependence of the bismuth luminescence intensity is briefly discussed.

I. INTRODUCTION

THE recombination of holes and electrons in wide-band-gap semiconductors can produce luminescence, often in the visible spectral region. Gallium phosphide is an extensively studied III-V semiconductor with an indirect gap $E_G \sim 2.34$ eV at $T \lesssim 20$°K. Recently identified radiative transitions in GaP include the decay of indirect excitons bound to the isoelectronic substitutional impurities nitrogen[1] and bismuth,[2] to neutral donors such as sulfur,[3] and to pairs of widely separated shallow donors and acceptors such as sulfur and carbon.[4] The transition energies are of the order of 0.1 eV below E_G, and the luminescence is therefore in the green-yellow region of the spectrum.

The internal quantum efficiency of photoluminescence due to these transitions increases with the concentration of the relevant impurity at low concentrations, and may approach unity at concentrations near 10^{17} cm^{-3} when competition from other inadvertently present recombination centers has been overcome.[5] An exception is the luminescence of excitons bound to neutral donors, where the luminescence efficiency does not exceed $\sim$0.2% because of competition with an Auger nonradiative process which takes place within the donor-exciton complex.[6] Except for the isoelectronic substituents, the luminescence efficiency decreases rapidly with increasing impurity concentration in the high concentration range, above $\sim 10^{18}$ cm^{-3}.[7]

Results of a study of the effect of sulfur donors on the efficiency of bismuth luminescence in solution grown GaP single crystals are reported in the present paper. This choice of impurities was made because the sulfur donor is an essentially nonradiative recombination center for free excitons at low temperatures as a result of the predominant Auger recombination process mentioned above. It therefore appeared that capture competition between the bismuth and sulfur centers for photoexcited free excitons or free holes and electrons would be easily recognized experimentally through an appropriate variation of the bismuth efficiency with increasing sulfur concentration. The experimental results reported here show that this variation is much more rapid than expected on the capture-competition model at high sulfur concentrations, but is consistent with an Auger quenching process involving the exciton bound to the bismuth center and a third electronic particle in an impurity band formed at the high-donor concentrations. Previously unpublished data on the low-temperature concentration quenching of donor-acceptor pair luminescence in GaP is also discussed and shown to be consistent with a similar model involving the migration of carriers through impurity bands formed by the majority impurity. Experimental results on the temperature dependence of the luminescence efficiency in double-doped crystals of GaP are also presented and

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[1] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).
[2] F. A. Trumbore, M. Gershenzon, and D. G. Thomas, Appl. Phys. Letters **9**, 4 (1966).
[3] P. J. Dean, Phys. Rev. **157**, 655 (1957).
[4] The type I_A green pair spectrum which is usually present in GaP grown from gallium solution was attributed to sulfur donors and silicon acceptors by D. G. Thomas, M. Gershenzon, and F. A. Trumbore [Phys. Rev. **133**, 26 (1964)]. Recent evidence, to be reported elsewhere, indicates that the shallow acceptor in this spectrum, ionization energy $\sim$48 meV, is due to carbon, not silicon.
[5] See Ref. 2 for bismuth luminescence; see M. Gershenzon and R. M. Mikulyak, Appl. Phys. Letters **8**, 245 (1966) for donor-acceptor pair luminescence in GaP.
[6] D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, Phys. Rev. Letters **17**, 1262 (1966).
[7] This is apparent, for example, in the effect of high concentrations of zinc on the red luminescence of zinc and oxygen double-doped GaP; see M. Gershenzon, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, J. Appl. Phys. **36**, 1528 (1965).

discussed from the viewpoint of the impurity-band–Auger (IBA) concentration quenching model.

II. EXPERIMENTAL CONSIDERATIONS

A. Crystals

The GaP single crystals were grown from gallium solution. Crystals containing bismuth as the only intentionally present impurity were prepared at 1100°C by reacting phosphine with gallium doped with 10% (atomic) bismuth.[8] Crystals containing both sulfur and bismuth were grown by cooling from 1100°C in sealed quartz capsules containing gallium doped with 10% bismuth and various amounts of sulfur as required to produce donor concentrations in the range from the lower limit of just below 10^{16} cm^{-3} in "sulfur-free" crystals to $\sim 10^{19}$ cm^{-3}.[9] The bismuth concentration was approximately constant at ~ 3 to 4×10^{17} cm^{-3}.[2,10] The neutral sulfur donor concentrations were estimated from the integrated area of the no-phonon absorption line at ~ 2.31 eV due to the creation of the exciton-neutral donor complex.[11] This absorption line becomes unmeasurably broad for $\gtrsim 2\times 10^{18}$ sulfur donors, so the neutral donor concentrations were estimated from the room-temperature surface-barrier capacitance[12] at the highest donor concentrations.

B. Luminescence and Absorption Measurements

The crystals were mounted in a double-wall gas-flow Dewar which enabled stable crystal temperatures in the range $T \gtrsim 15$°K to be attained by the suitable adjustment of the temperature and rate of flow of gas from a liquid-helium reservoir.[13] The luminescence was excited utilizing intrinsic absorption processes by focussed light from an Osram HBO 200-W mercury arc lamp, filtered by two Corning 7-59 glass filters. The photoluminescence was focussed through a Corning 3-70 filter onto the entrance slit of a Czerny-Turner $f/6.8$ $\frac{3}{4}$-m spectrometer fitted with an EM1 9558 Q/A photomultiplier held at -25°C in a thermoelectric cooler. The bismuth luminescence was also excited by direct absorption in the weak bismuth absorption bands[2] below E_G, using appropriately filtered exciting light from the mercury arc lamp. Optical absorption measurements were made using a tungsten strip filament light source. Luminescence excitation spectra utilizing nitrogen impurity and intrinsic interband absorption processes were recorded using a GE 650-W tungsten-iodine spectral source focussed directly onto the spectrometer. The emergent, nearly monochromatic light was focused onto the refrigerated sample and the resultant luminescence, suitably filtered to remove the exciting radiation, was collected by the photomultiplier mounted close to the Dewar window.

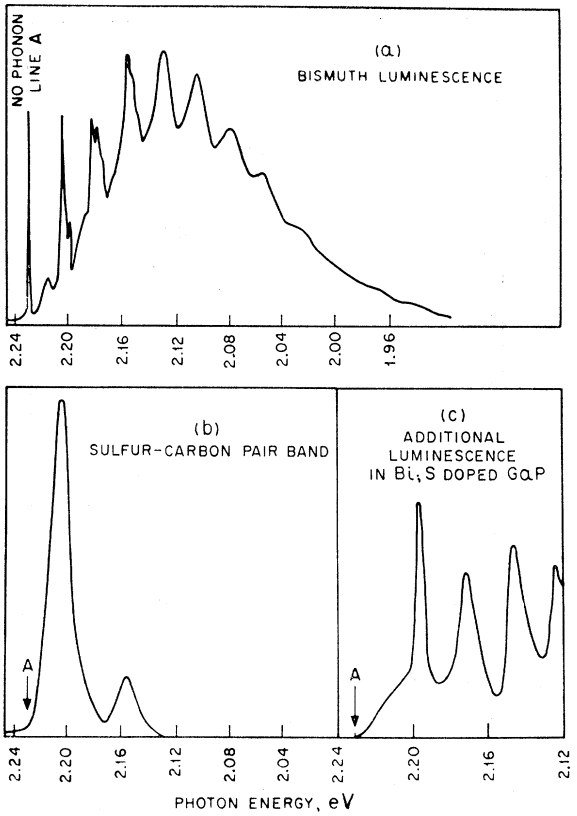

FIG. 1. Luminescence spectra observed from GaP crystals deliberately doped with sulphur and/or bismuth: (a) spectrum associated with the $A(\Delta J=1)$ exciton transition at bismuth isoelectronic traps (Ref. 2); (b) spectrum due to electron-hole recombination between sulfur donors and shallow carbon acceptors; and (c) a new spectrum attributed in Ref. 15 to electron-hole recombinations between sulfur donors and bismuth hole traps. Spectra (b) and (c) were usually relatively weak and superposed on (a) in the dc-excited spectra recorded in the present work.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Only the bismuth luminescence spectrum [Fig. 1(a)] was observed from the dilutely sulfur-doped crystals. The sulfur-carbon[4] donor-acceptor pair band [Fig. 1(b)] became evident at higher sulfur concentrations, and was quite strong in some crystals. There is a marked tendency towards a nearly constant compensation level of ~ 10 to $\sim 25\%$ in GaP.[14] An increase in the sulfur concentration in the crystals due to the deliberate

[8] R. T. Lynch (private communication).

[9] See, for example, J. F. Miller, in *Compound Semiconductors*, edited by R. K. Willardson and H. L. Goering (Reinhold Publishing Corp., New York, 1962), Vol. 1, Chap. 23.

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

[11] M. Gershenzon, 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.

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

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

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

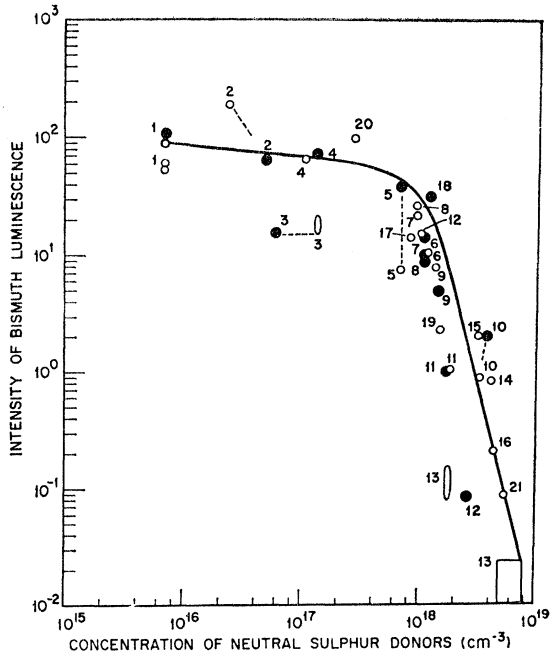

FIG. 2. Quenching of the bismuth luminescence recorded in GaP near 20°K [spectrum shown in Fig. 1(a)] by neutral sulphur donors. The smooth curve is an empirical fit to the experimental points. Note the relatively small effect below $\sim 10^{18}$-cm^{-3} sulphur donors and the dramatic quenching above this critical concentration. The integers denote different crystals. The displacement of points for the same crystal indicates the experimental reproducibility for small displacements and the possible variation between crystals obtained in the same growth run for the larger displacements. The filled circles were obtained from the experimental runs used for Fig. 4.

addition of sulfur to the gallium solution prior to crystal growth therefore probably resulted in an increase in the concentration of carbon acceptors inadvertently present. In addition, a new spectrum [Fig. 1(c)], with a relatively broad no-phonon line at 2.196 eV and phonon coupling very similar to that observed in the bismuth spectrum at 20°K, was observed superimposed on the bismuth spectrum of several relatively heavily sulfur-doped ($\sim 10^{18}$ cm^{-3}) crystals. The origin of this new spectrum is uncertain at present.[15]

The dependence of the low-temperature integrated bismuth luminescence intensity on the neutral sulfur concentration (Fig. 2) shows little decrease until the sharp drop starting near 10^{18} cm^{-3}. Differences in bismuth concentration and sample dimensions were neglected in Fig. 2. The former effect is expected to be small.[2] Effects of variable sample dimensions should be relatively unimportant since the penetration length of the exciting light was always considerably less than the crystal thickness, and the images of most crystals covered the entrance slit height of the spectrometer.

The luminescence of excitons bound to bismuth or sulfur impurities in GaP was observed to be a linear function of the excitation intensity under the conditions used in the present experiments. This is as expected in view of the short lifetimes measured for these exciton complexes[10] and the relatively low maximum excess electron-hole concentration ($\sim 10^{15}$ cm^{-3}) estimated from photo-Hall-effect measurements on the most pure crystals of GaP presently available.[16] Under these conditions, it is a straightforward matter to estimate the effects of capture competition of the neutral sulfur donors for the excess carriers on the intensity of the bismuth luminescence. Neglecting the donor-acceptor pair luminescence due to the sulfur donors and inadvertently present acceptors, this competition decreases the over-all luminescence efficiency of the crystals, since the neutral sulfur donors are predominantly radiationless recombination centers for free excitons.[6] The continuous curves in Fig. 3 are predictions of the dependence of the low-temperature bismuth luminescence efficiency on the neutral sulfur donor concentration based upon the simple capture-competition model, assuming various ratios between the capture cross

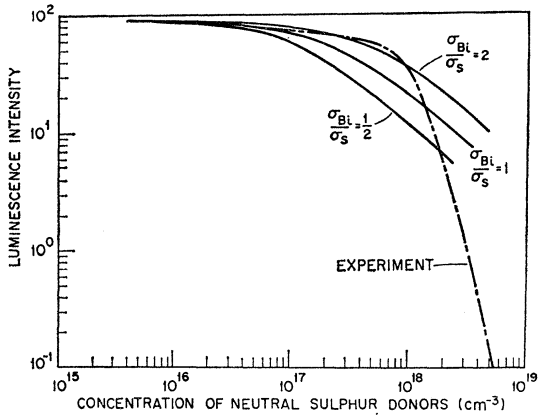

FIG. 3. The measured curve is from Fig. 2. The remaining curves show the reduction of the bismuth luminescence intensity anticipated if the only significant effect of the neutral sulphur donors on the bismuth luminescence intensity involves competition for the excited electron-hole pairs. Various relative capture cross sections of the bismuth traps and neutral sulphur donors have been assumed. Note that the knee in the experimental curve near 10^{18}-cm^{-3} neutral donors is not reproduced under this assumption.

[15] A probable interpretation is that it arises from the recombination of electrons at sulfur donors with holes on the bismuth isoelectronic traps. This inter-impurity transition has the special property that there is no Coulomb term in the recombination energy since the bismuth hole trap is uncharged. The phonon cooperation for the new spectrum is similar to that observed in the bismuth spectrum [compare Figs. 1(c) and 1(a)] as expected, since, according to the interpretation offered here, the phonon coupling should be predominantly due to the hole which is bound by short range forces to the bismuth atom (see Ref. 36). A similar recombination process has been recently reported in Zn (or Cd)-O double-doped GaP, although there the no-phonon remote pair transitions were not resolved from the strong vibronic sideband [C. H. Henry, P. J. Dean, and J. D. Cuthbert, Phys. Rev. **166**, 754 (1968)].

[16] H. C. Montgomery (private communication).

sections of the sulfur and bismuth centers for free excitons.[17]

The relatively sharp knee in the experimental curve near 10^{18}-cm^{-3} sulfur impurities, representing the onset of rapid quenching of the bismuth luminescence for further increase in the sulfur concentration, is not reproduced by the simple capture-competition model for any assumed ratio of the two capture cross sections.

The temperature dependence of the integrated bismuth luminescence intensity was also measured between ~ 20 and $\gtrsim 100$°K for most of the sulfur-doped crystals used for Fig. 2 (Fig. 4). The luminescence intensity of the sulfur-exciton complex is known to decrease by two orders of magnitude between 20 and 40°K in bismuth-free crystals, owing to thermal dissociation of this complex.[3] On the capture competition model, an increase in the bismuth luminescence efficiency is therefore predicted as the efficiency of the sulfur recombination center is reduced in this temperature range.[18] Figure 4 shows that the bismuth luminescence intensity is relatively temperature-independent below 40°K, however, even for sulfur concentrations which produce strong quenching at the lowest temperatures. Thus the temperature dependence of the bismuth luminescence intensity is inconsistent with an identification of the low-temperature quenching of the bismuth luminescence with capture competition between the bismuth and sulfur impurities.

It is shown in Sec. IV A that the most significant sulfur-induced quenching of bismuth occurs at and above the threshold sulfur concentration for metallic impurity-band conduction, where the sulfur-exciton complexes can no longer be regarded as noninteracting recombination centers. The overlap between adjacent

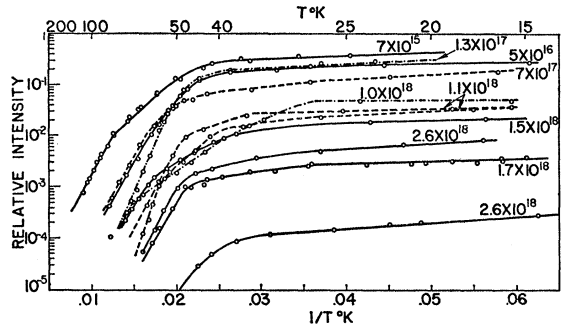

FIG. 4. The temperature dependence of the bismuth luminescence intensity for various GaP crystals containing the indicated concentrations of neutral sulphur donors. The luminescence was excited by interband absorption in the GaP host crystal.

[17] It should be remembered in this comparison of cross sections that the exciton-bismuth interaction occurs through the trapped hole (Ref. 36), whereas excitons are bound to the neutral sulphur donors by an electron pair bond (Ref. 3). The carrier of opposite type is believed not to bind alone to either of these centers. An alternative mechanism for the weak concentration quenching below $\sim 10^{18}$ cm^{-3} neutral donors is suggested in the Appendix.

[18] This effect is apparent in the temperature dependence of photoluminescence at deep pair states in GaP in the presence of shallow-donor-acceptor pair states (see, for example, Ref. 5).

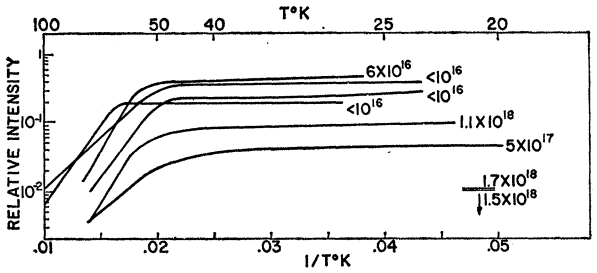

FIG. 5. The temperature dependence of the bismuth-luminescence intensity for various GaP crystals containing the indicated concentrations of neutral sulphur donors. The luminescence was excited by absorption at the bismuth impurity centers.

sulfur centers broadens the sulfur exciton absorption line near 2.31 eV. At 2×10^{18}-cm^{-3} sulfur donors the width of this line has increased to ~ 20 times the value for concentrations well below 10^{17} cm^{-3}.

No sulfur-exciton luminescence was detected at low temperatures from these sulfur-bismuth double-doped crystals for any value of the sulfur donor concentration. At very low sulfur concentrations the product of the concentration and the exciton capture cross section is negligible compared with this product for the $\sim 4\times 10^{17}$ cm^{-3} bismuth centers, and the bismuth internal luminescence efficiency approaches 100%. Sulfur concentrations sufficiently large for appreciable capture competition in crystals containing high concentrations of bismuth atoms (Fig. 2) are already in the range where exciton hopping between adjacent sulfur sites takes place, leading to the efficient transfer of the excitation to the bismuth or other relatively deep exciton traps. This effect has been observed at high nitrogen concentrations in GaP, where exciton luminescence at isolated nitrogen impurities is quenched by tunneling transfer to deeper states involving close pairs of nitrogen atoms.[1] Capture competition between bismuth and sulfur exciton traps should be more significant in crystals containing appreciably lower bismuth concentrations than used in the experiments reported in the present paper.

The capture competition model is therefore unable to account for the observed dependence of the bismuth luminescence efficiency on the sulfur concentration, or for the temperature dependence of the efficiency for different sulfur concentrations. Indeed, the experimental observations just described imply that capture competition was insignificant for the bismuth-sulfur double-doped GaP crystals used in this investigation. Capture competition between the bismuth and sulfur exciton traps should have a significant effect on the bismuth-luminescence efficiency in crystals containing appreciably lower bismuth concentrations, however. It will be shown in Sec. IV that the experimental results described above are consistent with the IBA model, which is the only apparent alternative to the capture-competition model.[19]

[19] It is shown in Sec. IV A that phonon-assisted impurity-band conduction processes should be efficient in GaP near 10^{18} cm^{-3} sulfur donors (see, also, Fig. 8).

Thermal quenching of the bismuth luminescence under excitation in the bismuth absorption band between ~2.33 and ~2.30 eV was also measured in crystals containing different sulfur concentrations. Since the bismuth absorption coefficient did not exceed 2 cm^{-1} and most of the crystals studied were $\lesssim 0.1$ cm thick, only a small specimen-dependent fraction of the intensity of the exciting radiation was absorbed. The relative intensity levels of the crystals used for Fig. 5 have been corrected for the effect of the specimen-dependent crystal thickness. The luminescence was weak, partly because of the incomplete absorption within the crystals, and the quenching above ~50°K in Fig. 5 could not be followed as far as in Fig. 4. The general trend in Fig. 5 is very similar to that in Fig. 4, however. In particular, the 20°K luminescence efficiencies of the heavily sulfur-doped crystals were again much smaller than those of the lightly sulfur-doped crystals. The neutral sulfur donors do not produce absorption in the excitation energy interval used in these measurements. This result therefore supports the view that the quenching effect of the neutral sulfur donors is not primarily due to their competition with the bismuth centers for the photo-excited excess carriers. On the contrary, since the bound excitons are produced by direct absorption processes at the bismuth centers in this experiment,[20] the results in Fig. 5 imply that, at a sufficient concentration of neutral sulfur donors, this excitation is removed by some nonradiative process involving the bismuth center itself.

In the past, measurements of the relative integrated intensity of shallow ("green") donor-acceptor pair luminescence in GaP have been made as a function of the concentration of the neutral donor (sulfur) measured by the techniques used in the present paper (Sec. II A). Previously unpublished data on the quenching of 20°K sulfur-carbon pair luminescence, due to Gershenzon and Trumbore, are compared in Fig. 6 with experimental points taken from Fig. 2. The trends established by the two sets of data are identical, namely that the luminescence quenching is a weak function of concentration at low-donor concentrations, but a rapid concentration-quenching rate occurs above ~10^{18}-cm^{-3} neutral donors. This similarity obtains even though the sulfur donor is involved in the radiative transition for pair luminescence, but not for bismuth luminescence.[21]

[20] Absorption coefficients for two-step absorption processes, by which sulfur-exciton complexes might be produced in this energy region, are negligible compared with even the weak absorption at the bismuth centers. It has been shown that donor-acceptor pair luminescence rather than bound exciton luminescence is predominant at the low excitation intensities available in two-step absorption processes: E. F. Gross and S. D. Nedzvetskii, Dokl. Akad. Nauk SSSR **152**, 1335 (1963) [English transl.: Soviet Phys.—Doklady **8**, 989 (1964)].

[21] The observation in Fig. 6 that the donor-acceptor pair radiative recombinations quench at the same rate with donor concentration as the bismuth luminescence explains why the bismuth luminescence is not completely obscured by the shallow-pair luminescence at high donor concentrations, an effect to be expected otherwise in view of the tendency towards a fixed level of compensation mentioned above.

The similar concentration quenching behavior of these two quite dissimilar types of radiative transitions strongly suggests that this quenching "threshold" is not determined from the properties of the luminescence centers themselves, but from the critical effect of an impurity concentration near 10^{18} cm^{-3} on the properties of the quenching impurity. It is also apparent that the concentration-quenching mechanism considered in this paper relates specifically to impurities which donate electrons (or holes) to the crystal. The luminescence efficiency of otherwise undoped GaP crystals containing $\gtrsim 10^{19}$-cm^{-3} isoelectronic nitrogen substituents can be as high as typical crystals containing ~10^{17} nitrogen atoms, even though rather low efficiencies are often observed at the highest nitrogen concentrations. These low efficiencies are therefore not a characteristic property of high concentrations of nitrogen impurities, but rather are believed to be an accidental byproduct of the efficient inter-nitrogen tunneling[1] which apparently results in the transfer of much of the excitation energy to deep recombination centers of unknown origin in many heavily nitrogen-doped crystals. By contrast, the efficiencies of all types of luminescence so far studied in GaP are *invariably* vanishingly small for concentrations of neutral donors or acceptors approaching 10^{19} cm^{-3}, as indicated in Fig. 2. These notions lead directly to the IBA model proposed in the next section.

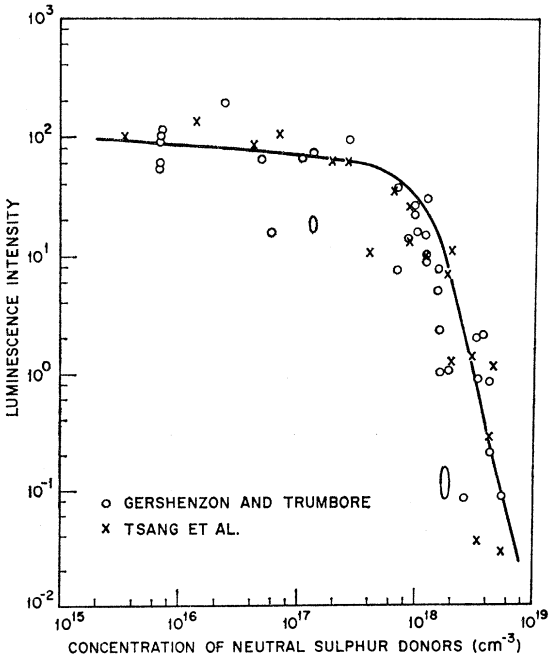

FIG. 6. Comparison between the dependence on the concentration of neutral sulphur donors of the intensities of sulphur-carbon shallow donor-acceptor pair luminescence (o points) and of bismuth-bound exciton luminescence (× points) measured in GaP at 20°K. The smooth curve is identical to that given in Fig. 2 and adequately represents both sets of experimental points.

IV. MODELS FOR CONCENTRATION QUENCHING: IMPURITY-BAND–AUGER MODEL

Two general mechanisms exist for the completely nonradiative recombination of excess electrons and holes. One involves the emission of the recombination energy in a multiphonon cascade. In a semiconductor like GaP, the energy gap E_G is much greater than $\hbar\omega_{\text{opt}}$. In general, the efficiency of this process can be competitive with the radiative recombination efficiency only if the transition energy is spanned by a series of real energy states with a maximum mutual energy separation equivalent to a few of the relevant phonons,[22] say $\sim$0.2 eV for the exciton recombination centers considered in the present paper. No such ladder is known to exist in GaP, and it is certain that one is not introduced by the impurities considered in this paper. The second possibility is some type of an Auger recombination in which three quasiparticles interact simultaneously, and the recombination energy of two of them is given to the third. The energy transferred is usually large enough to take the third particle deep into an allowed band of energies of the host crystal, and the excess energy can then be liberated by successive emission of single phonons connecting real electronic energy states within the band.[23]

An Auger process has been postulated[6] to account for absorption cross section, lifetime, and efficiency discrepancies in transitions involving an exciton bound to neutral sulfur donors in GaP, a system which involves two bound electrons and a bound hole. Bismuth introduces a bound exciton state involving only one electron and one hole, however. No Auger recombination process is possible for this complex and none is suggested by the properties of the electronic transition when bismuth is the only intentionally added impurity.[10] The simultaneous presence of high concentrations of sulfur donors introduces the possibility that electrons on a nearby donor may interact with excitons localized on bismuth substituents and thereby promote Auger recombinations. As the sulfur concentration increases, this process becomes more probable, not only because the mean bismuth-sulfur separation decreases, but more importantly because the donor electrons become delocalized into an impurity band and are then readily accessible at the bismuth exciton complexes. The lifetime and efficiency of the bismuth luminescence are then reduced and become limited by this impurity-band–Auger (IBA) recombination process, rather than by the radiative process.

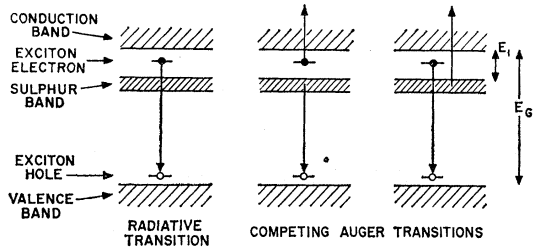

FIG. 7. A schematic representation of possible Auger transitions involving a bound exciton at the bismuth trap and an electron in the sulphur donor-impurity band. These transitions form the basis of the IBA recombination process introduced in the text.

Two different types of IBA transitions are possible for the sulfur-impurity-band–bismuth interacting system, as shown in Fig. 7. Since $E_I \ll E_G$, these two processes are considered equivalent in the simplified model calculation in Sec. IV B.

A. Sulfur Donor Impurity Band in GaP

Impurity-band conduction in semiconductors has been extensively studied in recent years.[24–26] Three different conduction mechanisms have been identified. At low concentrations the dominant process is phonon-assisted hopping of electrons between ionized centers. At intermediate concentrations it has been suggested that negatively charged H^--like states are formed, and the conduction occurs via electron wave-function overlap between the H^--like charged centers and nearby neutral centers.[27] At still higher concentrations, the ground states of the neutral impurity centers overlap sufficiently that the electrons and holes become delocalized and metallic conduction occurs within the resulting impurity band. This mechanism suggests that the metallic behavior should commence when the mean inter-impurity spacing is equal to twice the radius of the ground-state electron or hole orbit, $r_H \rightarrow a_H$. Studies in germanium and silicon have shown that this criterion is too restrictive, and Mott has argued, using the hydrogenic approximation, that the critical density N_M for the onset of metallic conduction obeys the relationship[25]

$$N_M^{1/3} a_H = 0.20. \quad (1)$$

Equation (1) implies that $N_M \sim 4\times10^{18}$ cm^{-3} for the sulfur donor in GaP, where $a_H \sim 12$ Å, according to the relationship $a=\hbar/(2m^*E)^{1/2}$, which is appropriate for noneffective masslike donors. The transverse mass $m_t^*=0.26\,m_0$ has been used to obtain this result, since this defines the maximum overlap of adjacent donor states. For the density-of-states mass $m^*\sim0.4\,m_0$, so that $a\sim10$ Å.[28]

[22] A. Kiel, in *Quantum Electronics*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), p. 765; also, M. J. Weber, Phys. Rev. **157**, 262 (1967).

[23] E. F. Smith and P. T. Landsberg, J. Phys. Chem. Solids **27**, 1727 (1966).

[24] H. Fritsche, J. Phys. Chem. Solids **6**, 69 (1958).

[25] N. F. Mott, Phil. Mag. **6**, 287 (1961).

[26] N. F. Mott and W. D. Twose, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1961), Vol. 10, p. 107.

[27] H. Nishimura, Phys. Rev. **138**, 815 (1965).

[28] R. A. Faulkner (private communication). These effective masses were obtained by numerical differentiation of the conduction-band structure calculated using the pseudo-potential form factors published by M. L. Cohen and T. K. Bergstresser [Phys. Rev. **141**, 789 (1966)]. The resulting value of m_c is in good agreement with that obtained from the $\mathbf{k}\cdot\mathbf{p}$ method by F. H. Pollak, C. W. Higginbotham, and M. Cardona, J. Phys. Soc. Japan Suppl. **21**, 20 (1966).

Hall measurements on sulfur-doped GaP indicate that the ionization energy E_D tends to zero for $N\sim5\times10^{19}$ cm^{-3}. Again, this is too stringent a criterion for the onset of metallic conduction.[24] Nishimura has suggested that the threshold for this condition should occur when the activation energy associated with conduction in the intermediate region vanishes.[27] The value of N_M obtained from this criterion for sulfur donors in GaP is $\sim5\times10^{18}$ cm^{-3}, in good agreement with the result obtained from Eq. (1).

There seems little doubt, then, that the onset of metallic impurity-band conductivity should occur at sulfur-donor concentrations near 5×10^{18} cm^{-3} in GaP. Indeed, the threshold donor concentrations for the various impurity conduction mechanisms listed above can be forecast for GaP from the literature data for germanium (Fig. 8) or silicon simply by scaling the concentrations according to the cube of the ratio of the donor orbits, in view of Eq. (1). Figure 8 shows that the hopping-type conductivity process is replaced by the intermediate mechanism involving the H^--like donor states at a concentration near 10^{18} cm^{-3} for shallow impurity states such as the sulfur donor in GaP. Recent experimental measurements of the Hall coefficient and conductivity of sulfur-doped GaP confirm that impurity conduction processes become significant above $\sim10^{18}$ cm^{-3} neutral donors, although no detailed distinction was made between the "hopping" and "intermediate" regimes of impurity conduction.[29,30]

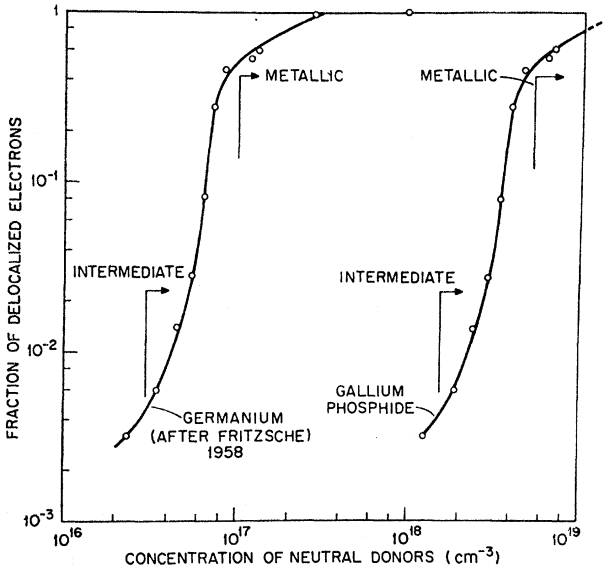

FIG. 8. The dependence of the fraction of electrons which may be regarded as delocalized on the concentration of neutral antimony donors in germanium and on the concentration of neutral sulphur donors in GaP. For germanium, the experimental points were obtained from measurements of the Hall coefficient at 2.5°K made by Fritsche (Ref. 24). The curve for GaP was calculated from the germanium data by altering the concentration scale in the ratio $N_{GaP}/N_{Ge}=(a_H)^3_{Ge}/(a_H)^3_{GaP}$ according to Ref. 25. In this relationship $(a_H)_{Ge}$ and $(a_H)_{GaP}$ were taken to be, respectively, 45 and 12 Å.

B. Auger Effect Involving One Free Carrier in GaP

Tolpygo, Tolpygo, and Sheinkman have considered an Auger process involving a free hole and two bound electrons on a pair of interacting neutral donors in a recent theoretical discussion of some photoconductive effects in germanium and GaAs.[31] They claim that the hole-capture cross section can be large if the donors associate, since a significant increase in the wave-function overlap of the bound electrons can then occur. The fact that one electron and the hole are bound to a point defect produces a favorably large electron-hole wave-function overlap for the IBA process in GaP considered in the present paper.

An order of magnitude calculation of the efficiency of the IBA recombination process can be obtained from the observed properties of the sulfur donor complex in GaP[6] if the Auger coefficient[32] is assumed to depend predominantly upon the mean concentration of the second electron over the volume occupied by the bound exciton.[33,34] The concentration of each electron in the sulfur-exciton complex is equivalent to an average electron concentration N_{av} throughout the crystal of $\sim10^{19}$ cm^{-3}, assuming that the electron orbits have a characteristic radius $a=\hbar/(2m^*E)^{1/2}$, where E is the binding energy. The corresponding Auger coefficient α is 500.[6] For an electron (donor) concentration N_{del}, which is equal to N_D-N_A above the threshold N_M for complete delocalization, the internal bismuth luminescence efficiency η_L should therefore be given from

$$\eta_{L0}=\eta_L+\eta_{Auger}=\eta_L+\alpha\frac{N_{del}}{N_{av}}\eta_L \qquad (2)$$

so that

$$(\eta_L/\eta_{L0})=[1+\alpha N_{del}/N_{av}]^{-1}. \qquad (3)$$

The internal luminescence efficiency at a donor concentration well below N_M is represented by η_{L0} in Eqs. (2) and (3). Below N_M, the appropriate value of N_{del} in Eq. (3) is the concentration of delocalized electrons (see Fig. 8).

The form of this relationship cannot be checked very closely in the present work since N_M is large $\sim5\times10^{18}$ cm^{-3} (Sec. IV A) and because of the statistical spread

[29] T. Miyauchi, H. Sonomura, and N. Yamamoto, Japan. J. Appl. Phys. 6, 1409 (1967).

[30] M. M. Cohen and F. D. Bedard, J. Appl. Phys. 39, 75 (1968).

[31] E. I. Tolpygo, K. B. Tolpygo, and M. K. Sheinkman, Fiz. Tverd. Tela 7, 1790 (1965) [English transl.: Soviet Phys.—Solid State 7, 1442 (1965)].

[32] The Auger coefficient α is the ratio of the Auger (nonradiative) and the radiative transition probabilities.

[33] The Auger transition considered in the IBA recombination process should be very similar to that discussed in Ref. 6, since an *electron* is ejected into the conduction band with nearly the same kinetic energy in both of these transitions.

[34] The authors are indebted to C. H. Henry for this qualitative comparison between these two Auger processes.

in the data in Figs. 2 and 6. However, for $N=5\times10^{18}$ cm^{-3} (i.e., near N_M) and $\alpha=500$, Eq. (2) predicts that $\eta_L/\eta_{L0}\sim0.4\%$, a value reasonably consistent with the experimental results in Figs. 2 and 6. For bismuth-exciton and shallow donor-acceptor pair luminescence in GaP, η_{L0} is close to unity at the low temperature used in Figs. 2 and 6.[2,5]

A rigorous *a priori* calculation of the probability for the IBA transitions shown in Fig. 7 is rendered difficult by the indirect nature of the exciton transition. An additional difficulty is the fact that the high energy of the recoiling electron ($\sim E_G$) necessitates a detailed knowledge and consideration of the conduction band structure of GaP to nearly E_G above the indirect conduction band minima at the [100]-type boundaries of the reduced zone. A simplified model was therefore considered whereby the true conduction band structure was replaced by a hypothetical nondegenerate parabolic conduction band located at the center of the reduced zone E_G above the valence band maximum. The impurity band located close below the minimum of this single conduction band was assumed to be of negligible width compared with E_G. Bloch functions were used for all but the exciton particles, which were given hydrogenic $1s$ envelope functions $G_i(r)$, where $i=c$ or v in the effective mass approximation $\chi_i=u_i(\mathbf{k}_i,\mathbf{r})G_i(\mathbf{r})$. The effective masses m_c and m_v in the conduction band c and valence band v were taken as the geometric means of the relevant mass parameters, and are $\sim0.46m_0$ for electrons[28] and $0.80m_0$ for holes,[28] where m_0 is the free electron mass. The Auger inverse recombination lifetime $1/\tau_A$ was then calculated using Fermi's golden rule of perturbation theory, taking as the perturbation the Coulomb interactions between the two electrons and considering exchange effects for the electrons. The resulting expression is

$$1/\tau_A=C_AG_A, \tag{4}$$

where $C_A=8\sqrt{2}(e^4/m_0^{1/2})\sim3.09\times10^{-5}$ [eV$^{3/2}$ sec^{-1}] (5)

and

$$G_A=\left[\frac{8}{(x+1/x)^3}\right]^2\frac{(m_0/m_c)^{1/2}|F_1F_2|^2}{\{1+(m_0/m_v)[(E_G/R_H)/(x+1/x)^2]\}^4}\times\frac{N_{\rm del}}{\epsilon^2E_G^{3/2}}[\text{eV}^{-3/2}],\quad x\equiv\left(\frac{m_c}{m_v}\right)^{1/2}. \tag{6}$$

In Eq. (6) R_H is the Rydberg (13.6 eV), ϵ the static dielectric constant [11.1 (Ref. 35)], $N_{\rm del}$ the concentration of delocalized electrons in the impurity band, and F_1F_2 is a product of overlap integrals of the modulating part of the Bloch functions $u(\mathbf{k},r)$ given by[36]

$$F_1=\frac{1}{v}\int_v u_c^*(\mathbf{k}_c,\mathbf{r})u_v(\mathbf{k}_v,\mathbf{r})d\mathbf{r},$$
$$F_2=\frac{1}{v}\int_v u_I^*(\mathbf{k}_I,\mathbf{r})u_c(\mathbf{k}_c,\mathbf{r})d\mathbf{r}. \tag{7}$$

[35] A. S. Barker, Jr., Phys. Rev. **165**, 917 (1968).

In Eq. (7) subscript I refers to the donor impurity band. According to Equations (4) to (6), the Auger recombination time in GaP is given by

$$\tau_A=\frac{10^7}{|F_1F_2|^2N_{\rm del}}\ \text{sec}. \tag{8}$$

The Auger transition rate depends not only upon the density of final states available to Auger electrons "selected by the energy conservation requirement" but also upon the matrix elements for the Coulomb interaction between Bloch functions at the relevant points within the reduced zone. The conduction bands of a crystal in the extended zone scheme are quite similar to a free-electron parabola if the effect of the crystal field on the energy bands is not profound. Thus the Auger rate calculated as above on the basis of a simple parabolic conduction band should fairly adequately account for the effects of both energy conservation and the transition matrix elements. Appreciable deviations from the predictions of the simple theory are possible when the crystal field has a considerable influence on the electronic energy bands, as it does in GaP. The magnitude and direction of this influence depends critically upon the position of the final state energy of the Auger electron within the energy band structure of the real crystal.

The empirical radiative recombination time τ_R is close to 10^{-6} sec for the allowed exciton recombinations at the bismuth center.[10] Thus for $N_{\rm del}=5\times10^{18}$ cm^{-3} and $\tau_A/\tau_R=\eta_L/\eta_{L0}\sim10^{-3}$ (Figs. 2 and 6), Eq. (8) gives $|F_1F_2|^2\sim0.002$. Previous studies of $|F_1F_2|^2$ for direct gap semiconductors[36] suggest values of the order of magnitude 0.1. The much smaller value obtained from the present results arises mainly because the radiative transition rate is greatly reduced for *indirect* transitions. The radiative rate for *direct* transitions can also be calculated on the above simplified model.[37] Then

$$1/\tau_R=C_RG_R, \tag{9}$$

where

$$C_R=e^2/3m_0\hbar^2c^3=0.72\times10^7[\text{eV}^{-2}\ \text{sec}^{-1}] \tag{10}$$

and

$$G_R=\left[\frac{8}{(x+1/x)^3}\right]^2\left(\frac{m_0}{m_c}-1\right)\mu E_G^2[\text{eV}^2], \tag{11}$$

where μ is the refractive index of GaP near the bismuth luminescence band.

With $|F_1F_2|^2=0.1$, $N_{\rm del}=5\times10^{18}$ cm^{-3}, Eqs. (8) and (9) predict

$$\tau_A=2\times10^{-11}\ \text{sec},\quad \tau_R=9\times10^{-9}\ \text{sec},\quad \tau_A/\tau_R=2\times10^{-3}.$$

Experimentally, the radiative recombination time for

[36] P. T. Landsberg, in *Lectures in Theoretical Physics* (University of Colorado Press, Boulder, Colo., 1966), Vol. 8A, Sec. 6.

[37] Equation D17 of P. T. Landsberg [*Problems in Recombination Statistics, Festkoerperprobleme, VI* (Frederick Vieweg und Sohn, Brounschweig, Germany, 1967)] was used as the basis for this calculation of radiative transition rate.

the allowed exciton recombinations at the bismuth center is of order 10^{-6} sec, and Figs. 2 and 6 suggest a luminescence efficiency $\eta_L/\eta_{L0}\sim10^{-3}$. Thus if the Auger effect is responsible for the nonradiative transitions, the following empirical results are obtained:

$$\tau_A/\tau_R\sim\eta_L/\eta_{L0}\sim10^{-3}.$$

Thus $\tau_A\sim10^{-9}$ sec if $\tau_R\sim10^{-6}$ sec.

The closeness of the theoretical estimate of τ_A/τ_R to this empirical result acts as a check on the validity of the IBA model.

C. Temperature Dependence of the Luminescence Efficiency

At donor concentrations below the intermediate impurity-conduction region (i.e., $<10^{18}$ cm^{-3}) less, than 0.1% of the donor electrons are delocalized according to Fig. 8. Eq. (3) shows that the IBA quenching at low temperatures should then be negligible. The temperature dependence of η_L shown in Fig. 4 for the bismuth-exciton complex in relatively dilutely sulfur-doped GaP crystals is similar to that reported in Ref. (2). Above $\sim$80°K, the luminescence efficiency exhibits a close to exponential decrease with increasing temperature, and the activation energy for this process is near 50 meV for most crystals. The mechanism of this quenching is not understood in detail. For sulfur donor concentrations near 10^{16} cm^{-3}, the number of free electrons produced by thermal ionization at 80°K is $\sim10^{13}$ cm^{-3}. This is far too small to induce a significant free carrier Auger recombination channel according to the discussion in Sec. IV B.

The only alternative quenching mechanisms apparent are either thermal dissociation of the bismuth-exciton complex itself, or a temperature dependence of the capture cross section. The magnitude of the thermal activation energy is inconsistent with expectation ($\sim$107 meV) for thermal dissociation of the bismuth-exciton complex in n-type crystals. On the second model, a 50-meV activation energy might represent the thermal ionization of electrons trapped by Bi^+ centers.

It should be particularly noted that the temperature quenching curves for the relatively heavily sulfur-doped crystals, where $\eta_L\ll\eta_{L0}$ at low temperatures, do not approach the efficiency-temperature curves for the most lightly sulfur-doped crystals at the highest temperatures reached in these experiments (Fig. 4). This is contrary to expectation if the 50-meV activation energy quenching process is independent of the sulfur-donor concentration, as suggested above, and is an effect which lacks explanation at present.

V. SUMMARY

The efficiency η_L of low temperature ($\sim$20°K) near bandgap photoluminescence in GaP is a rapidly decreasing function of the concentration of neutral donors (or acceptors) above a rather sharply defined threshold near 10^{18} cm^{-3} impurity atoms. This effect occurs well below the temperature range in which η_L is significantly temperature-dependent. The observed form of the dependence of η_L on the impurity concentration cannot be reproduced by capture-competition models, and is not sensitive to the nature of the luminescent center. Concentration quenching begins close to the threshold concentration ($\sim1\times10^{18}$ cm^{-3}) predicted for intermediate-type impurity-band conduction according to the models developed by Mott and Nishimura and also according to an appropriate scaling of experimental results obtained for germanium by Fritsche. Recent experimental studies of electrical transport properties in GaP[29,30] also indicate the onset of impurity conduction processes above $\sim10^{18}$-cm^{-3} neutral donors. The quenching is a very rapidly increasing function of concentration near the threshold N_M for metallic impurity-band conduction ($\sim5\times10^{18}$ cm^{-3}). The rapidly varying concentration-induced reduction in η_L for this concentration region can be interpreted on an IBA model. According to the IBA model, the delocalized carriers in the impurity band interact with the excited luminescent centers and are promoted to the continuum energy states of the GaP crystal through the absorption of all the recombination energy. On this model, η_L is reciprocally related to the concentration of delocalized (metallic) carriers $N_{\rm del}$ well above the quenching threshold (i.e., near N_M). The IBA luminescence quenching model is consistent with the observation of efficient luminescence in GaP containing very high concentrations ($\gtrsim10^{19}$ cm^{-3}) of isoelectronic substituents when the concentrations of neutral donors and acceptors are well below the limit for impurity band formation.

Calculations based upon the Auger coefficient observed in the luminescence of excitons bound to neutral donors in GaP and independent calculations based upon simplified models of the radiative and Auger recombinations both indicate that free carrier concentrations $\gtrsim$ a few times 10^{16} cm^{-3} are necessary to produce significant reductions in η_L. Since $N_{\rm del}$ is a very rapid function of the impurity concentration, and only approaches the latter near N_M, the observed rapid onset of strong quenching near N_M follows from the IBA model. In addition, the experimental observation that η_L is only weakly temperature dependent below 40°K, even when η_L has been lowered by two orders of magnitude by concentration quenching, is readily understandable, since $N_{\rm del}$ is temperature-independent above N_M.

Thermal quenching of η_L for bismuth occurs both in heavily and lightly sulphur-doped GaP above $\sim$40°K. The activation energy for thermal quenching, particularly that at high temperatures ($\gtrsim$80°K in lightly sulfur doped crystals) is insensitive to the donor concentration. The magnitude of this latter activation energy ($\sim$50 meV) and the details of this temperature-quenching mechanism are not completely understood,

although thermal ejection of electrons from the bismuth donors may be involved.

ACKNOWLEDGMENTS

The authors have benefited from numerous conversations with R. A. Faulkner, C. H. Henry, and D. G. Thomas concerning effects described in this paper. The original impetus for these experiments was provided by D. G. Thomas. Thanks are due to F. A. Trumbore for making available unpublished data on concentration quenching of shallow donor-acceptor pair luminescence in GaP and for a number of discussions of this material, and to R. T. Lynch for the GaP crystals used in this work.

APPENDIX

The impurity-band–Auger model presented in this paper depends upon the notion that delocalized electrons contribute much more effectively to Auger recombinations at randomly distributed recombination centers than electrons localized at donor impurities. Henry[38] has recently pointed out that if *neutral* donors (as opposed to donor sites) are distributed uniformly, the Auger recombination rate due to the electrons associated with these centers should be identical to the Auger rate due to an equal number of electrons in the conduction band, or in an impurity band. This follows since the electron probability density evaluated at a random point, e.g., at a radiative recombination center, is simply N_D-N_A, the average electron density within the crystal, and since the binding energy of the donor electron is negligible compared with the band gap energy. In view of the experimental evidence for the important role of impurity banding in the concentration quenching produced by neutral donors, we are forced to conclude that the assumption of a uniform distribution of *neutral* donors is incorrect in an excited crystal at low temperatures and at concentrations below the limit for impurity banding. The uniform neutral-donor distribution produced by cooling such a crystal in the dark from 300°K to well below the carrier freeze-out temperature (i.e., $\ll$100°K) will be disturbed through the influence of the Auger process under interband photoexcitation. Electrons ejected from neutral donors into the conduction band by Auger recombination processee will be recaptured at ionized donors independent of the proximity of bismuth traps. The probability of reejection is much higher for an electron trapped at a donor close to a bismuth trap, however, and the over-all effect of these capture and ejection processes is to weight the electron distribution towards remote donors and so to reduce the importance of the Auger process itself. The ionized donors near the bismuth radiative centers are compensated by the inadvertently present carbon acceptors.

Henry has shown that the effective fraction of the electron population available for Auger recombinations is only a few percent of N_D-N_A, assuming localized donor states and the sulfur donor and bismuth concentrations used in the present work with a compensation level of 20%. The dependence of the luminescence intensity on the neutral donor concentration is correspondingly weak [see Eq. (3)], approximately of the order shown below $\sim 10^{18}$ cm^{-3} in Figs. 2, 3, and 6. It is therefore possible that this reduced Auger process is partly responsible for the observed concentration quenching below 10^{18} cm^{-3} neutral sulfur donors, rather than the capture competition effect discussed in Sec. III. At low temperatures and high donor concentrations, impurity banding will increase the effective electron concentration to the full amount N_D-N_A, and the concentration quenching is accounted for by the IBA model described in Sec. IV. At low donor concentrations, the electrons from the uncompensated donors can only become fully effective in the Auger radiationless recombination process at temperatures sufficiently high to cause appreciable ionization of the donor states. This thermal-ionization-induced enhancement of the Auger effect in compensated crystals should be important at room temperature. Preliminary evidence for this process in gallium phosphide has been obtained by Welber, Morgan, and Scardefield.[39]

[38] C. H. Henry (private communication).

[39] B. Welber, T. N. Morgan, and J. E. Scardefield, Bull. Am. Phys. Soc. 12, 383 (1967).