$(-\hbar^2/2M)$ are negligible as discussed in the text. For the second term on the right-hand side of (C4), the term $g'=g$ gives unity. However, the term $g''=g$ gives the contribution

$$J_{l,l+h}\langle\chi_l^0|\chi_{l+h}^0\rangle C_{l+h}\,, \qquad \text{(C5)}$$

which is the only essential modification of (2.5). The vibrational overlap integral is essentially of the form[26]

$$\langle\chi_l^0|\chi_{l+h}^0\rangle=\exp\{-(E_b/\hbar\omega_0)\}\,,$$

where E_b is the binding energy. Since one would expect that

$$E_b \lesssim \hbar\omega_0$$

the above factor is less than, but of the order of, unity. Had the analysis been carried out at finite temperatures, the above factor would essentially get replaced by[26]

$$\exp\{-(E_b/\hbar\omega_0)(1+2\bar{N})\}\,,$$

where, however,

$$\bar{N}=(e^{\hbar\omega_0/k_0T}-1)^{-1}\,,$$

the average number of phonons at temperature T is exponentially small. These arguments, it is felt, verify the conclusions drawn in the text.

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PHYSICAL REVIEW VOLUME 140, NUMBER 5A 29 NOVEMBER 1965

Time-Decay Characteristics of a Deep-Donor–Shallow-Acceptor Pair Band in Gallium Phosphide

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Characteristics of the photoluminescent time decay of a red band at 1.82 eV (20°K) in GaP crystals doped with varying amounts of the shallow acceptor Zn and the deep donor O were studied. The red-band decay is nonexponential in time, shortens with increasing zinc concentration (the concentrated dopant), is nearly independent of the oxygen concentration (the dilute dopant), is essentially constant in shape and magnitude at low temperatures, shifts to lower frequencies during decay, and is not dependent on photoconductivity during decay. These observations are in accord with the model of pair-band decay and so support the interpretation of Gershenzon *et al.* that the red band at 1.82 eV (20°K) is a Zn-O pair band.

INTRODUCTION

A NUMBER of years ago it was proposed that radiative recombination would occur between electrons trapped on donor atoms and holes trapped on acceptor atoms.[1–4] More recently, such radiation has been positively identified in GaP for shallow-donor–shallow-acceptor pairs.[5–7] The identification resulted from the observation of scores of sharp emission lines in the green which were found to obey

$$h\nu_i=E_G-E_D-E_A+e^2/\epsilon r_i, \qquad (1)$$

where $h\nu_i$ is the photon energy of the ith donor-acceptor pair emission line, E_G the band gap energy, E_D and E_A the donor and acceptor binding energies, and $e^2/\epsilon r_i$ the Coulombic interaction energy of the ith pair. Since lattice sites have discrete separations, the pair separation r_i is "quantized" and so yields the many discrete emission lines. For separations greater than 40 Å the discrete lines merge into a broad band.[6]

The decay of this broad band in GaP has been studied[8–10] and found to be nonexponential in time. This has been explained by Thomas, Hopfield, *et al.*[8,9] assuming that the donors and acceptors are distributed randomly in the crystal and that the probability of radiative decay of a pair depends on the separation r as $\exp(-r/R)$, where R is comparable to half the Bohr radius of the more weakly bound one of the pair. This model is essentially the same as that proposed by Hoogenstratten[2] to explain the slow decay in ZnS. Specific predictions[8,9] of the time decay of the entire pair band have been made for the conditions of all donors and acceptors initially neutral, extreme dilution of either the donor or acceptor, and no mobility of captured electrons or holes. These predictions are that the shape and height of the decay curves will be inde-

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[1] J. S. Prener and F. E. Williams, Phys. Rev. **101**, 1427 (1956); J. Electrochem. Soc. **103**, 342 (1956).

[2] W. Hoogenstratten, Philips Res. Rept. **13**, 515 (1958) (see Chap. 3, Secs. 11 and 12).

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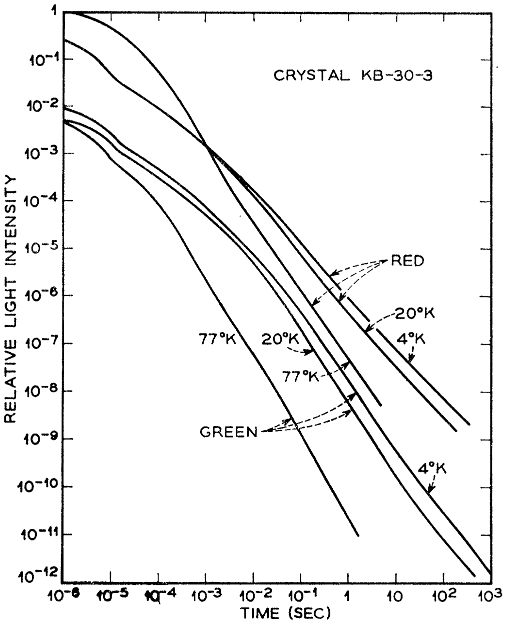

FIG. 1. Decay of the red fluorescence (which peaks at 1.82 eV at 20°K) of GaP containing an "optimum" doping of Zn and O following photoexcitation. The curves for different temperatures are plotted in the correct relation to each other. However, the curves for the green Zn-S pair band present in the same crystal are not normalized to the red decay curves. Over 100 experimental points were used in drawing each curve. (This is also true for Figs. 2 and 3.) The zero of time was taken at the peak of the excitation pulse.

pendent of temperature at temperatures where thermal ionization is negligible and that the decay shape will depend only on the majority impurity. This theory also predicts that the emission band will shift to lower photon energies during decay because of the faster decay of the closer pairs which emit at higher energies. These effects have been observed for the shallow-donor–shallow-acceptor pair bands in the green region.[8–10]

Besides the green pair emission from GaP, there are emission bands frequently seen at longer wavelengths, especially in the red region. These bands are many times broader than the green pair bands and do not have any discrete pair lines on the high-frequency side of the bands, facts which may be explained by either enhanced phonon cooperation or a broadened distribution of energy states. In spite of these prominent differences from the green pair bands, the red bands have been identified as being deep-donor–shallow-acceptor pair bands by Gershenzon *et al.*[11] Their evidence for this assignment consists of a strong correlation between the intensity of one of these red bands (and no other band) with the concentration of the deep-donor oxygen and the shallow-acceptor zinc. They also found that the band shifted by the difference in acceptor binding energies, consistent with Eq. (1), when zinc was replaced with cadmium.

Since broad featureless emission bands, perhaps similar to the red band in GaP, are a common observation in semiconductors and phosphors, it is of interest to examine other properties of the red band in order to confirm its pair-band designation. We report here observations of its photoluminescent time decay at various temperatures and Zn and O concentrations, on the absence of photoconductivity during decay, and of the shift of the band as seen by time-resolved spectra taken during decay. These observations are in accord with the pair band model[2,8,9] and exclude a previously proposed model[12] of nonexponential decay in phosphors.

EXPERIMENTAL TECHNIQUE

The crystals used in this study[13] were grown by the slow cooling of saturated solutions of GaP in gallium[6] containing various amounts of either Zn, Ga_2O_3, or ZnO, and are the *same* crystals used in the study by Gershenzon *et al.*[11]

Excitation for the time-decay measurements was furnished by an EGG FX-12 xenon flash lamp supplied by a 1.5J electrical pulse from a 0.16-μF capacitor. This gave a flash length of about 3 μsec with a detectable tail for another 7 μsec. The latter makes the decay curves somewhat uncertain for the first few μsec and probably accounts for the bump seen there on some of the decay curves. A mirror collected 0.84 sr of the lamp emission and focused it on the GaP which was immersed in either liquid nitrogen, hydrogen, or helium. Filters guaranteed that only light of photon energies greater than those of the band gap impinged on the GaP. The fluorescent light passed through the GaP before entering the spectrometer. Self-absorption of fluorescence at the wavelengths and temperatures used, however, introduces a negligible error. For measuring the time decay of the entire red band, the fluorescence was directed through a Corning 2-61 filter to an RCA 7326 photomultiplier. Since the decay was nearly power law in form, larger *RC* products in the photomultiplier anode circuit could be used at longer decay times, which thus enabled the decaying light signal to be traced to 10^{-9} or 10^{-10} times its initial height.

For measuring the spectrum at particular times following the decay, the flash lamp was repetitively pulsed. The fluorescence from the GaP was sent through a Perkin-Elmer monochromator to the RCA 7326 photomultiplier. Its signal was fed into a Hewlett-Packard 185B sampling oscilloscope whose display at a particular delay time was fed into a chart recorder whose drive represented the wavelength drive of the monochromator. The considerable photon noise on the signal arising from the short sampling time of the oscilloscope (0.5 nsec) was greatly reduced by a suitable *RC* integrating circuit on its input without distorting the decay at the delay times studied. The system response

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[11] M. Gershenzon, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, J. Appl. Phys. **36**, 1528 (1965).

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[13] Crystals were grown by F. A. Trumbore.

(relative signal per incident photon) was determined as a function of wavelength using a tungsten filament of known temperature as a black-body radiator, and the recorded fluorescent signal from the GaP was corrected accordingly. Because of the great breadth of the red band (0.147 eV), it was necessary to multiply the measured fluorescent intensity per unit wavelength by $d\lambda/d\nu$ before plotting it as intensity per unit photon energy.

TIME-DECAY RESULTS

Photoluminescent-decay curves are shown in Fig. 1 at temperatures of 77, 20, and 4.2°K for a GaP crystal grown from a melt doped with 10^{-1} at. % Zn and 10^{-2} mole % Ga_2O_3. These melt concentrations correspond[14] to 1.5×10^{18} Zn atoms cm^{-3} and an unknown amount of O in the crystal; they yield crystals with the highest efficiency in the Zn-O pair band[11] and so are called "optimized" concentrations. The crystal also contains some sulphur as an unintentional dopant. This leads to the presence of the green Zn-S pair band[6,7] whose decay is also shown in Fig. 1 for comparison.

Several things are to be noted concerning the red light decay. First, the decays are far from exponential in shape. At low temperatures the decay approximates a t^{-1} dependence. Second, the heights of the curves are substantially identical at low temperatures. Third, as the temperature is lowered, the decay of the red becomes slower. For a green pair band this has been shown[15] to be due to a reduction of thermal ionization of the trapped holes at the lower temperatures and of the more tightly bound electrons at higher temperatures. This explanation should also apply to the red pair band. Note that for the red decay, the shapes of the decay curves are identical at 20 and 4.2°K for short times, during which thermal ionization is negligible, and the curves differ by only a factor of two after decaying a factor of 10^8. The decay of the red band was also examined at 196 and 297°K. At 196°K it was slightly slower than the flash lamp fall off but could not be measured accurately, and at 297°K it followed the decay of the flash lamp.

Though these facts are qualitatively in accord with the pair band model,[8,9] a quantitative comparison with the Hopfield predictions cannot be made since all of the Zn-O pairs are not filled initially by the flash lamp even when operated at full power. Two experiments done on an "optimized" crystal (KB30-3) of Figs. 1 and 4 indicate this. First, the intensity of the red band increases linearly with excitation intensity up to the highest flash intensities used at 77°K (and at 297°K also) indicating, we believe, a lack of saturation of the red pairs. At 20°K the red band was superlinear with excitation intensity due to the saturation of the highly efficient[11] green pair band that was also present. Such saturation, which leads to a sublinear dependence of fluorescence on excitation, is often observed in the green pair bands when the pair constituents are at the level of unintentional impurities. Second, the decay curve was studied as the excitation was reduced and it was found to continually change shape, particularly at short times after excitation. A constant shape of the decay curve for a range of high excitation intensities would have indicated saturation.[9] On the other hand, a quantitative comparison with the Hoogenstratten model does not seem possible because of its assumption of mobility (via a hopping-type process) of one type of carrier. Such conduction is not present in these crystals as can be seen from their exceedingly high resistivity at low temperature (see the Photoconductivity Search section).

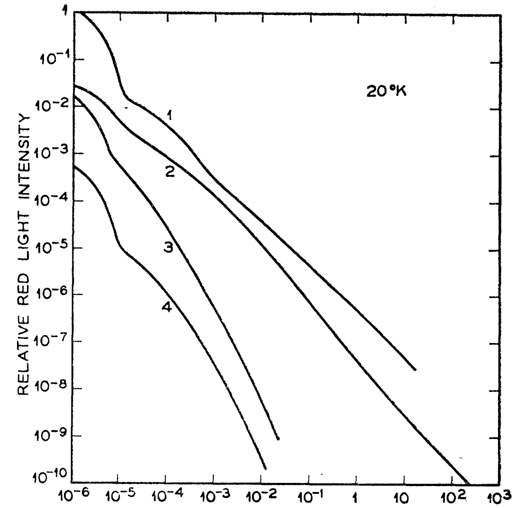

FIG. 2. Decay of the 1.82 eV red band in GaP at 20°K for the following melt dopings: 10^{-2} mole % Ga_2O_3 plus (1) 10^{-3} at.% Zn, (2) 10^{-1} at.% Zn, (3) 1 at.% Zn, and (4) 10 at.% Zn. The curves are not normalized to each other.

We have also measured the decay of the red band in crystals of different Zn and O concentrations at 20°K. Since all the crystals are strongly p type, we know that the Zn is the majority impurity. Increasing its concentration should shorten the decay according to the pair band model.[2,8,9] Figure 2, in fact, shows this to be the case. On the other hand, since O is the minority constituent, an increase in its concentration should have no appreciable effect on the shape of the decay until the crystal becomes nearly compensated. Figure 3 shows the decay of four crystals grown from melts containing various Ga_2O_3 dopings, and it can be seen that the decay does not change appreciably between the crystals. In fact, the change in the decays between the two most heavily doped crystals is towards lower decay slope for the more heavily doped crystal. This may be due to partial compensation[9] or to nonradiative recombination from close pairs which would normally emit at the short

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[14] F. A. Trumbore, H. G. White, M. Kowalchik, R. A. Logan, and C. L. Luke, J. Electrochem. Soc. **112**, 782 (1965).

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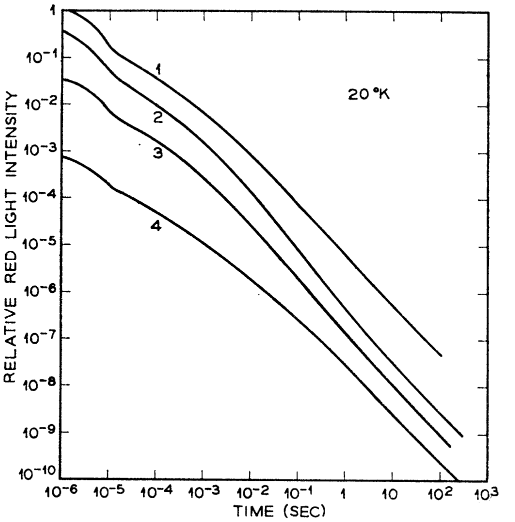

FIG. 3. Decay of the 1.82 eV red band in GaP at 20°K for the following melt dopings: 10^{-1} at.% Zn plus (1) no intentionally added O, (2) 10^{-2} mole % GaO_3, (3) 10^{-1} mole % Ga_2O_3, and (4) 1 mole % Ga_2O_3. The curves are not normalized to each other.

decay times. (The over-all luminescent efficiency is known to be lower for this doping level.[11])

TIME-RESOLVED SPECTRA

Time-resolved spectra of the red band were measured to see if the band moved to lower photon energies during decay. This is expected by the pair-band model since the closer pairs, which emit at higher photon energies, decay more rapidly than the more distant pairs, which emit at lower photon energies. A shift of 0.012 eV has been observed for the green pair band during decay.[8,9] Spectra of the red band at various delay times after the peak of the excitation pulse are shown in Fig. 4 for an "optimized" Zn-O doped crystal at 20°K. Because of the much larger breadth of the red band (0.147 eV) compared with the green pair bands (~0.025 eV), it is much harder to observe the shift. The shift of the red band in Fig. 4 is, in fact, most easily seen by looking at the position of the half intensity points. These are seen to shift to lower photon energy by 0.009 eV on the average during decay.

PHOTOCONDUCTIVITY SEARCH

The nonexponential decay of pair band luminescence does not depend on photoconductivity in any way. In fact, in the simplest formulation[8,9] of the decay thermal ionization of trapped electrons and holes into conducting states has been neglected. We have looked for photoconductivity during the luminescent decay following xenon flash lamp excitation of a GaP crystal having the optimum Zn-O doping. Contacts were made by evaporating 2000 Å of Au containing 0.05% Be onto the crystal held at 650°C followed by 5000 Å of Au. At 20°K the *I-V* characteristic was nearly ohmic (corresponding to $7.5\times10^4\Omega$ cm resistivity) particularly at the higher biases (20 to 50 V) used in searching for a long photoconductivity decay. At 4.2°K the resistivity was greater than $6.5\times10^9\Omega$ cm. At 4.2°K the photoconductivity decayed with the excitation intensity and no evidence of photoconductivity after 10 μsec could be found. At 20°K the *positive* photoconductivity was also found to decay with the excitation intensity. However, at this temperature a *negative* photoconductivity followed the excitation pulse. The crystal resistivity rose to 1.4×10^5 Ω cm and the excess resistivity then decayed nonexponentially by a factor of 100 in a period of 1 sec. The effect was shown not to be a property of the external circuit or measuring instruments. Since this effect reduces the number of holes, which is already very small compared to the number of Zn atoms, it cannot cause any appreciable redistribution of trapped holes during luminescent decay. An understanding of this last effect must await further experiments. It is clear, however, that it is not the cause of the long nonexponential light decay but only a small perturbation on it at 20°K.

DISCUSSION

The data presented show the red band decay to be nonexponential in time, to shorten with increasing Zn concentration (the concentrated dopant), to be nearly

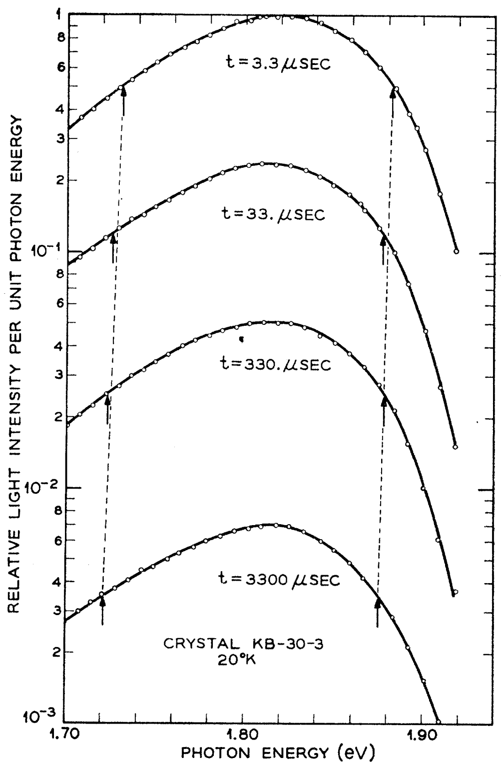

FIG. 4. Spectra, corrected for system response, of the red band in GaP crystal containing an "optimum" doping of Zn and O at 20°K at different delay times following the peak of the excitation pulse. The curves are properly normalized to each other.

independent of O concentration (the dilute dopant), to be essentially constant in shape and height at low temperatures, to shift to lower frequencies during decay, and not to be dependent on photoconductivity during the decay. These observations are in accord with the model[2,8,9] of pair-band decay and thus give strong support to the designation of the red band studied in GaP as a Zn-O pair band.

In the past, two other theoretical models have been proposed to explain nonexponential decays. One is the well known bimolecular decay law for the intensity $I=I_0/(1\text{-}t\beta n_0)^2$, where I_0 is the initial fluorescence intensity, β is the probability of recombination (units of cm^3/sec), and n_0 is the initial excitation density of either carrier. Since this must lead to a t^{-2} decay law for long times, it is clearly not relevant here. The second model[12] is based on the hypothesis that the rate of recombination is determined by the rate of release of carriers from traps and not by the probability of radiative recombination. This mechanism requires several steps: creation of nonequilibrium carriers, their capture in traps which have a distribution of binding energies, thermal release of the carriers from the traps into conduction states, transport, capture by the luminescent centers, and finally radiative recombination. This model is capable of predicting power law decays depending on the trap distribution. For a uniform distribution of traps which are initially all filled, the fluorescence decay would follow $NkT(1\text{-}e^{-st})/t$ (if retrapping is excluded), where N is the number of traps per unit energy, k is Boltzman's constant, T is the absolute temperature, and s is the rate constant of detrapping. For $st\gg 1$ the decay follows t^{-1}. For an initially filled exponential distribution of traps ($N=Ae^{-\alpha E}$), the decay would follow $f(\alpha,s,T)t^{-(\alpha kT+1)}$ for $st\gg 1$. Other trap distributions would give other decay functions. This model requires a photocurrent decay which parallels the fluorescence decay, predicts that the initial fluorescence level will be strongly temperature-dependent, and provides no mechanism for the shift to lower frequencies of the emission band during decay. The present observations on the red band in GaP are inconsistent with these requirements and thus exclude this model.

ACKNOWLEDGMENTS

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Open-Orbit Resonances in Tin*

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We have studied the resonant absorption of ultrasonic waves by electrons executing open orbits in pure single crystals of tin at low temperatures. Two types of resonance were observed, associated with periodic and aperiodic open orbits. The resonant oscillations arising from periodic open orbits in the [110] directions have a period consistent with the zone dimensions and generally narrow with increasing ultrasonic frequency as predicted by the theory. Some of these resonances, however, have an anomalous line shape, caused by interference with geometric oscillations. The other type of resonance is associated with generally aperiodic open orbits on the zone 4(a) hole Fermi surface. These resonant oscillations generally have a short period which varies rapidly with magnetic-field direction and is consistent with the zone dimensions. The width of the resonances decreases anomalously slowly with ultrasonic frequency, probably because of an inherent width associated with the aperiodicity of the orbits.

I. INTRODUCTION

THE interaction between acoustic waves and the conduction electrons in a metal in the presence of a magnetic field is a complex phenomenon which may give valuable information about the electrons (see Mackintosh[1] for a recent review). The experiments reported in this paper formed part of a rather comprehensive study of magnetoacoustic effects in tin.[2]

The resonant absorption of acoustic waves in a metal, when the period of an open orbit in the direction of propagation of the wave is a multiple of the wavelength, was first observed in tin and explained by Galkin, Kaner, and Korolyuk.[3] A number of further examples of open-orbit resonances have been observed,

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