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Kinetics of Radiative Recombination at Randomly Distributed Donors and Acceptors

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The kinetics of the recombination of holes trapped on acceptors with electrons trapped on donors have been treated theoretically and the results compared with the observed low-temperature fluorescent decay of GaP doped with sulphur donors and silicon acceptors. The assumptions are made that the distribution of donors and acceptors is random and that the recombination rate depends exponentially on the donor and acceptor separation. The theoretical problem can be exactly solved when either the donor or acceptor is in excess, and an approximate solution is given for the case of exact compensation. The decay of the total pair emission has been measured over many factors of 10 of intensity and time and can be satisfactorily accounted for by the theory using only two adjustable parameters. If the decay occurs from a system in which all the donors and acceptors are not initially neutral, different decay curves are obtained which can be explained by assuming that the capture cross section of a pair for a hole or electron depends approximately on the square of the internuclear pair separation. The spectra have also been measured after flash excitation, and they are found to change in shape and position as a function of time. These changes can be quantitatively explained in terms of the simple theory, provided residual broadening effects from phonon interactions and other sources are included. The effects of a magnetic field at low temperature on the decay kinetics have been predicted and observed and allow the determination of certain g values. At high-impurity concentrations there are deviations from simple behavior, evidently caused by complications in the chemical doping of the crystals. Experimental evidence for pair effects in the edge emission of CdS is also briefly reported. It is likely that similar decay phenomena observed in other seniconductors and phosphors can be explained on a similar basis without invoking arbitrary trap distributions. It is only necessary to assume a random distribution of donors and acceptors throughout the crystal.

I. INTRODUCTION

THE radiative recombination of electrons trapped on donors with holes trapped on acceptors is an important mechanism of light emission from semiconductors. The idea has been applied to fluorescence in ZnS and related compounds[1] and theoretical discussions have been given of the dependence of the recombination energy on the distance between the donor and the acceptor.[2] Direct proof of the existence of this pair emission was provided by the sharp line fluorescence from gallium phosphide, which was unambiguously interpreted as being due to pair effects.[3-5] For pairs of reasonably large separation, the energy of emission $E(r)$ is approximately given by

$$E(r)=E_{\text{gap}}-(E_a+E_d)+e^2/\epsilon r\,, \tag{1}$$

where E_{gap} is the band-gap energy, E_a and E_d are the acceptor and donor binding energies, respectively, ϵ is the low-frequency dielectric constant and r is the donor-acceptor separation. Since the donors and acceptors must fall on lattice sites only certain values of r are permitted and so line spectra can occur. As the donor-acceptor separation increases the lines tend to merge into a continuum. At the same time the lifetimes of the states become steadily longer. It has been realized that the long and variable lifetimes of the distant pairs could qualitatively account for long and nonexponential decay curves of the fluorescence after pulse excitation. In addition changes in the spectra as a function of the exciting intensity and variation of the decay kinetics with variation of the concentrations of the impurities can also be qualitatively understood in the same terms. Some or all of these points have been made in connection with GaP,[4,6-8] Si,[9] CdS,[6] and Ge,[10] and an outline of a

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[1] E. F. Apple and F. E. Williams, J. Electrochem. Soc. **106**, 224 (1959); J. S. Prener and F. E. Williams, Phys. Rev. **101**, 1427 (1956).

[2] F. E. Williams, J. Phys. Chem. Solids **12**, 265 (1960); W. Hoogenstraaten, Philips Res. Rept. **13**, 515 (1958).

[3] J. J. Hopfield, D. G. Thomas, and M. Gershenzon, Phys. Rev. Letters **10**, 162 (1963).

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

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

[6] D. G. Thomas, J. J. Hopfield, and K. Colbow, in *International Conference on the Physics of Semiconductors, Radiative Recombination* (Dunod Cie., Paris, 1964), p. 67.

[7] E. F. Gross and D. S. Nedzvetsky, Doklady Akad. Nauk SSSR **152**, 309 (1963).

[8] E. F. Gross and D. S. Nedzvetsky, in *International Conference on the Physics of Semiconductors, Radiative Recombination* (Dunod Cie., Paris, 1964), p. 81.

[9] A. Honig and R. Enck, in *International Conference on the Physics of Semiconductors, Radiative Recombination* (Dunod Cie., Paris, 1964), p. 113.

[10] C. Benoit a la Guillaume and J. Cernogora, in *International Conference on the Physics of Semiconductors, Radiative Recombination* (Dunod Cie., Paris, 1964), p. 121.

quantitative theory has been given.[6] It is the purpose of this paper to give a quantitative model for the decay kinetics and compare the predictions of this model with experimental results obtained from GaP.

In Sec. II the theory of the recombination rate is discussed and several statistical problems are solved in which the recombination rate is combined with random-impurity distributions. The treatment is different for the case in which the donors and acceptors are present in different concentrations, and for the case in which the donors and acceptors have similar concentrations. Calculations are made for the total-light-decay kinetics (i.e., the decay of all the pair radiation), and also for the change of spectral output at various times after flash excitation. The results of a variety of experiments chosen to provide a quantitative comparison to theory are presented and discussed in Sec. III.

An important result is that the total-light-decay curves are nonexponential, and over certain regions, approximate power laws. At low temperatures the curves are independent of temperature. These characteristics are not infrequently found in phosphor decays and have not hitherto received a satisfactory explanation. It is likely, therefore, that the results presented here may have rather wide application and may be used to establish the presence of pair spectra when the sharp lines cannot be seen.

II. THEORY

A. Introduction

The calculation of the time decay of the fluorescent spectra due to donor-acceptor pairs is treated as follows. The calculation of the decay rate of an isolated pair as a function of separation is basic to the problem. Given this, a statistical problem can then be defined to calculate the time decay and time-decay spectrum starting from some initial condition. The simplest initial condition which can be well defined theoretically and experimentally is that of all donors and acceptors neutral. The effect of a nonsaturated starting point, in which the different capture cross sections for different donor and acceptor configurations influence time-decay calculations is also investigated. An approximate treatment is given for the situation in which the donors and acceptors have the same concentrations.

B. The Calculation of the Rate of Decay of an Isolated Pair as a Function of Separation

The calculation of the radiative recombination rate $W(r)$ of an electron bound on a donor with a hole bound on an acceptor at a distance r from the donor, involves as its only "unknown" the optical (momentum) matrix element between the state of the crystal with the electron and hole present and the state with them absent. The first problem then is the finding of an adequate electron-hole wave function.

In general a Heitler-London approximation is certainly a bad one for the present problem, for the same reason that it is unsatisfactory for calculating the exchange between two hydrogen atoms.[11] To eliminate the need for such an approximation, we will consider only the case in which one particle (for definiteness, the hole) has a much smaller ionization energy than the other, a case appropriate for Si-S pairs in GaP. In this case, the wave function of the tightly bound particle is "rigid," and the hole sees no perturbation due to the neutral donor except in a volume of space small compared to the extent of the hole wave function. In this small volume the hole wave function will be considerably perturbed. Because of the strong binding of the electron, however, a product wave function (including the donor perturbation in the Hamiltonian of the hole) will be an adequate approximation.

The optical matrix element $M(r)$ for a product wave function is proportional to[12,13]

$$M(r)=\int\psi_1(r_h)[\mathbf{P}\psi_2(r_e)]\delta(\mathbf{r}_e-r_h)d^3r_e\,, \qquad (2)$$

where $\psi_1(r_h)$ is the vacant (i.e., hole) wave function and $\psi_2(r_e)$ is the electron wave function. The bracket is large only in the small volume occupied by the donor wave function. In this region, $\psi_1(r_h)$ is not simple. If it is assumed that the hole wave function in the *absence* of the donor does not vary appreciably over the region of the donor, then the problem can be simplified. In this case, and if the distance to the acceptor is not too small, the donor sees an incident hole wave of negative energy having a value and derivative (on a sphere circumscribed about the donor) proportional to the value of $\psi_1(r_h)$ at $r_h=r$ in the absence of the donor. The calculation of $\psi_1(r_h)$ in the region of interest is made no simpler by this observation, but it is seen to scale with a quantity $\psi_1^*(r_h)$, which is taken to be the wave function of the hole at the location of the donor in the absence of the donor. Thus

$$M(r)=\text{const}\times\psi_1^*(r)\,, \qquad (3)$$

where the constant unfortunately involves much detailed knowledge of donor states and band structure. Other factors being equal, this constant should be orders of magnitude larger in CdS than in GaP, for the indirect band gap of GaP prevents the major component of donor wave function from contributing to $M(\mathbf{r})$ except through phonon coupling.

The behavior of $\psi_1(r)$ for large r is simply expressible in terms of the binding energy E_a of the acceptor, and the ideal binding energy E_{H} of a hydrogenic acceptor

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[11] C. Herring and M. Flicker, Phys. Rev. **134**, A362 (1964).

[12] J. Shaffer and F. E. Williams in, *International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 811.

[13] J. J. Hopfield, *International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 725.

and is

$$\psi_1(r) \propto r^m \exp(-r/a)\,, \tag{4}$$

where

$$a=[(2m_h E)/\hbar^2]^{1/2}, \quad m=-1+(E_\mathrm{H}/E_a)^{1/2}. \tag{5}$$

In CdS (where the weakly bound particle is the *electron*), most simple donors are hydrogenic. For these, m will be zero, a will be the donor Bohr radius, and $W(r)$, proportional to $|M|^2$, will have the form,

$$W(r)=W_{\max}\exp[-r/R_d]\,, \tag{6}$$

with $W_{\max}$ a constant, and R_d half the donor Bohr radius. In GaP, Si is the shallowest known simple acceptor, having a binding energy of about 0.04 eV. Thus it is expected that for Si, the effective-mass approximation should be fairly good, and that Eq. (6) should also hold for GaP Si-S pairs, with a $W_{\max}$ different from CdS, and a R_d of half the acceptor Bohr radius.

In systems having known deviations from ideal behavior, Eqs. (4) and (5) might be used to make corrections. We have used (6), as it should be a good approximation, and have taken R_d as an independent parameter which is to be compared to its value determined from the binding energy. This comparison is complicated by the degenerate valence band in GaP.

In both GaP and CdS, $W(r)$ is permitted to be anisotropic as a result of band anisotropies. In CdS the donor anisotropy is known to be small—the electron mass and dielectric constant are very nearly isotropic. In GaP, the relatively low energy of the $\mathbf{k}=0$, Γ_1 conduction-band minimum should make the warping of the hole band small (like Ge rather than Si) and the acceptor relatively isotropic. The calculation expected to be most seriously afflicted by the neglect of this anisotropy is the calculation of the time-decay spectrum. The problem is most clearly illustrated by the fact that in the idealized theory, an isolated pair giving light at energy, E, must have a particular separation to give this energy, and therefore a particular decay rate. The 1:1 correspondence between decay rate and energy for isolated pairs is destroyed (broadened is perhaps a better description) by anisotropy of the decay rate.

Finally, in the approximation described the decay constant for a given pair will not be materially altered by the presence of another neutral donor within the fringes of the hole wave function. Two donors interacting with a given acceptor will simply produce two decay channels.

C. Calculation of the Total Light Decay. Donor or Acceptor in Excess. All Initially Neutral

The time decay of the fluorescence of an isolated initially neutral donor surrounded by a random distribution of neutral acceptors can be exactly calculated. Let the number of acceptors be N, the volume of the crystal V. Given a particular configuration of acceptors at positions r_j and a donor at the origin, there are N parallel decay channels for the electron to transfer itself from donor to acceptor. If Q is the probability that the electron is on the donor,

$$dQ/dt=-Q\sum_j W(r_j) \tag{7}$$

and

$$Q(t)=\exp(-\sum_j W(r_j)t)\,. \tag{8}$$

Of interest in an experiment on a large number of pairs is not (8) for a particular configuration, but rather the ensemble average, denoted by $\langle\ \rangle$, of (8). This can be obtained by multiplying (8) by the probability of a given configuration and summing over all configurations. Since each acceptor is randomly located in the volume V, the probability density for any acceptor is $1/V$, independent of position, and the ensemble average is given by

$$\langle Q(t)\rangle=\left(\frac{1}{V}\right)^N\int_V\int\cdots\int\exp\{-\sum_j W(n_j)t\} \times d^3r_1\cdots d^3r_j\cdots d^3r_N\,, \tag{9}$$

or

$$\langle Q(t)\rangle=\left[\frac{1}{V}\int_V \exp[-W(r)t]d^3r\right]^N. \tag{10}$$

For large r, $W(r)$ goes rapidly to zero. The exponential term can be rewritten as

$$\exp[-W(r)t]=1+\{\exp[-W(r)t]-1\}\,, \tag{11}$$

where the bracket goes rapidly to zero for large r. Thus,

$$\langle Q(t)\rangle=\left[1+\frac{4\pi}{V}\int_0^\infty\{\exp[-W(r)t]-1\}r^2dr\right]^N. \tag{12}$$

In the limit $N\rightarrow\infty$, $V\rightarrow\infty$, but $N/V=n$, the concentration, remains finite, and one finds

$$\langle Q(t)\rangle=\exp\left[4\pi n\int_0^\infty\{\exp[-W(r)t]-1\}r^2dr\right]. \tag{13}$$

The intensity $I(t)$ of light emitted at time t is

$$I(t)=-\frac{d}{dt}\langle Q(t)\rangle = \left\{4\pi n\int_0^\infty W(r)\exp[-W(r)t]r^2dr\right\} \times\left\{\exp\left[4\pi n\int_0^\infty\{\exp[-W(r)t]-1\}r^2dr\right]\right\}. \tag{14}$$

n, the concentration of the majority constituent, is referred to below as N_d and N_a when it refers to acceptors and donors, respectively.

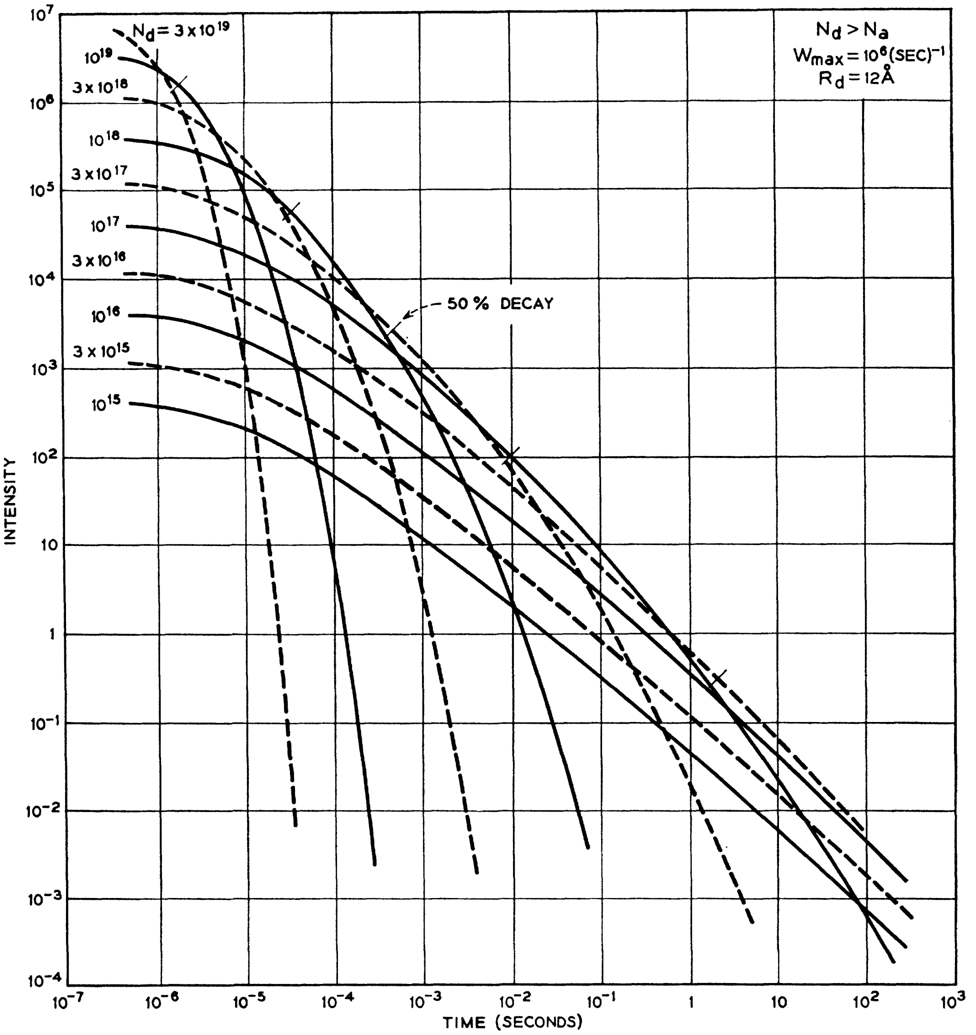

FIG. 1. Theoretical total-light-decay curves for the values of W_{max} and R_d indicated and for several donor concentrations. It is assumed that the donor concentration N_d exceeds the acceptor concentration N_a. The times at which half the holes have reacted are marked for some of the curves.

Given $W(r)$, this treatment is an exact treatment of the statistical problem in the limit of a large ratio of donor/acceptor concentrations (or acceptor/donor, *mutatis mutandis*). Equations (13) and (14) were programmed on an IBM 7090 for the form of $W(r)$ already discussed [Eq. (6)] and the results are shown in Fig. 1. In this figure are plotted the total-light-decay curves for several values of n for arbitrarily chosen values of R_d and W_{max}. $Q(t)$ is a function of only two parameters in this approximation, $(W_{max}\times t)$ and nR_d^3. Similarly, $I(t)/W_{max}$ is a function only of these two parameters. Particularly important is that there is only one parameter which sets the time scale, namely W_{max}, so that a necessary scaling law exists between $I(t)$ and W_{max}. When W_{max} is replaced by fW_{max} (but all else remains fixed) on a log-log plot with increasing intensities plotted vertically and increasing times to the right, this scaling law results in a simple displacement of the curves down and to the right (along a 45° line), each by an amount f. The existence of this scaling law is a consequence of the single time parameter W_{max}, and does not depend on a solution to the statistical problem.

D. Calculation of Spectra as a Function of Time. Donor or Acceptor in Excess. All Initially Neutral

For an isolated distant pair, the energy of recombination is given by Eq. (1). The presence of other charged impurities can lead to sizeable Coulomb corrections to this expression. Other *neutral* impurities do not have long-range Coulomb effects. For a single donor and many acceptors, all neutral, if the electron on the donor recombined with a hole on an acceptor a distance r away, the energy would be given in lowest order by Eq. (1), independent of the other acceptors. This fact permits one to calculate the *spectrum* as a function of time when the ratio of concentrations is large.

Taking the zero of energy as $E_{gap}-E_d-E_a$, a pair having a separation r produces light of energy

$$E(r)=e^2/\epsilon r. \tag{15}$$

The situation in which light occurs at a given energy E is one in which one acceptor (labeled for definiteness acceptor 1) is a distance given by Eq. (15) from the donor, and the other $N-1$ acceptors have some particular set of positions. The time decay of the occupancy of the donor is then,

$$Q_E(t)=\exp[-W(r_1)t]\exp\{-\sum_{j\neq 1} W(r_j)t\}. \quad (16)$$

The intensity $J_E(t)$ at energy E is due only to decays in which acceptor 1 is used in the recombination, so is given by

$$J_E(t)=W(r_1)\exp[-W(r_1)t]\exp\{-\sum_{j\neq 1} W(r_j)t\}. \quad (17)$$

The time decay observed is the ensemble average of (17) over all possible positions of the $N-1$ acceptors. The positions of these acceptors are independent of the existence of acceptor 1. In the limit of $N\rightarrow\infty$, the averages over N or $N-1$ acceptors are equivalent. The ensemble average is then the same as (8), so

$$\langle J_E(t)\rangle=W(r_1)\exp[-W(r_1)t]\langle Q(t)\rangle. \quad (18)$$

This expression gives the time dependence of the intensity emitted at energy E, where r_1 is given by (15). The number of acceptors between r and $r+dr$ is $4\pi r^2 n dr$. A distance range dr corresponds to an energy range,

$$dE=(e^2/\epsilon r^2)dr. \quad (19)$$

Thus, $I_E(t)$, the intensity/unit energy at energy E and time t is given by,

$$I_E(t)=\langle J_E(t)\rangle(e^2/\epsilon)^3 4\pi n/E^4, \quad (20)$$

or finally, combining (20), (15), and (6),

$$I_E(t)=4\pi n(e^2/\epsilon)^3\frac{1}{E^4}W_{\max}\left\{\exp\left[-\frac{e^2}{\epsilon E R_d}-W_{\max}\times t\exp\left\{-\frac{e^2}{\epsilon E R_d}\right\}\right]\right\}\langle Q(t)\rangle. \quad (21)$$

This expression then gives the time-decay spectrum. The only concentration dependences are the leading factor of the concentration dependence of $Q(t)$. The *shape* of the spectrum at a given time is therefore concentration-independent. So far it has been assumed that a given pair only radiates at an energy given by Eq. (1). The results of such a calculation are presented in Fig. 11 and discussed in Sec. IVC. In practice, phonon wings must be included on each no-phonon line. Equation (21) is used as the basis of this complete calculation and some results are given in Fig. 12.

E. Calculation of the Total Light Decay. All Initially Neutral. Donor and Acceptor Concentrations Equal

When donor and acceptor concentrations are comparable, the calculation of the time decay is more difficult. The fact that each donor electron does not have an independent transition, but instead has its possible hole states partially filled by earlier decays of other donors makes the statistical problem much more complicated. The major physical effect can be easily seen by considering an exactly compensated sample. After 99.9% of the pairs have recombined, the average separation of remaining occupied pairs, which should be more or less randomly located, will be ten times as large as it was at time zero, and the effective concentration will then be very small. The major statistical effect at long times comes from the fact that some neutral donors become isolated by the recombination of holes on near-neighbor acceptors with electrons on other donors.

To make statistics easier, consider only electrons. Let $f(N_i,M_j,t)$ be the probability density for having $N_1, N_2, \cdots, N_i$ electrons on sites $1, 2, \cdots, i$, and M_j electrons on site j, where sites j are acceptors and sites i are donors, and t is the time. At zero time, all the electrons are on donors. Random quantum-mechanical transitions are made in which electrons are transferred from atom i to atom j (if i has an electron and j does not) at a rate W_{ij} (the W_{ij} are separation-dependent). The allowed values of N_i or M_j are zero and one; at a particular time, a particular atom either has one or zero electrons. From the master equation for this Markoff process can be obtained a hierarchy of equations for expectation values averaged over the random transitions. If $\langle\ \rangle_{\text{av}}$ means the average over the random transitions, the first of these equations is

$$\begin{aligned}\frac{d}{dt}\langle N_i\rangle_{\text{av}}&=-\sum_j W_{ij}\langle N_i(1-M_j)\rangle_{\text{av}}\\&=\sum_j W_{ij}(\langle N_i\rangle_{\text{av}}-\langle N_iM_j\rangle_{\text{av}}). \quad (22)\end{aligned}$$

The average $\langle N_iM_j\rangle_{\text{av}}$ is not the same as $\langle N_i\rangle_{\text{av}}\langle M_j\rangle_{\text{av}}$, so this equation is not self-contained. The second equation would express $\langle N_iM_j\rangle_{\text{av}}$ in terms of already defined quantities and more complicated quantities.

The special case already treated, that of a single electron, single donor, and many acceptors is tractable by virtue of the fact that the single electron cannot both be on site i and on site j. Thus N_iM_j is always zero, and its average $\langle N_iM_j\rangle_{\text{av}}$ also zero. In this case Eq. (22) reduces to Eq. (7) with the notational change $N_i\rightarrow Q$ and is solvable. As soon as the concentrations of donors and acceptors are comparable N_iM_j can depart from zero.

The Hartree approximation to (22) is to replace the average $\langle N_iM_j\rangle_{\text{av}}$ in (22) by the product $\langle N_i\rangle_{\text{av}}\langle M_j\rangle_{\text{av}}$. This approximation neglects correlations in occupations, but does take into account the mean decrease in concentration of holes available to each electron with time. The Hartree approximation to (22) is correct for the following conditions: (a) in the limit of very different

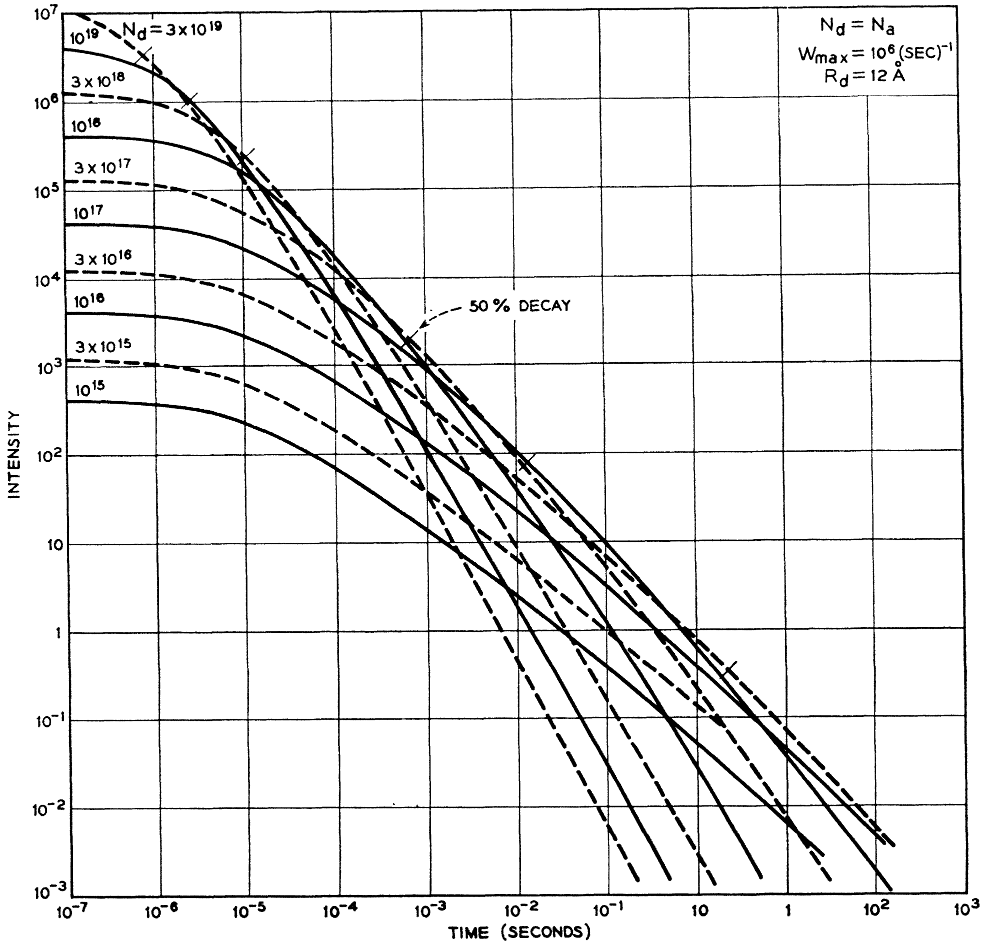

FIG. 2. The same as Fig. 1 except that $N_d = N_a$. Note that at sufficiently long times the intensity varies as $(\text{time})^{-2}$.

concentrations, for $\langle M_j \rangle_{\text{av}}$ approaches zero at all times in this limit; (b) in the limit of concentrations sufficiently large and times sufficiently short that many holes are present in a sphere of radius R_d.

The most extreme case, exact compensation, has for its solution in the Hartree approximation the implicit equation

$$\langle Q(t)\rangle_{\text{comp}} = \exp\left\{4\pi n \int_0^\infty \left(\exp\left\{-W(r)\times\int_0^t \langle Q(t)\rangle_{\text{comp}} dt\right\} - 1\right) r^2 dr\right\} ; \quad (23)$$

comp here indicating the exactly compensated case. Equation (23) is readily solved by noting that

$$\langle Q(t)\rangle_{\text{comp}} = \langle Q(\tau)\rangle , \quad (24)$$

where

$$\tau = \int_0^T \langle Q(t)\rangle_{\text{comp}} dt .$$

Thus,

$$d\tau/dt = \langle Q(t)\rangle_{\text{comp}} = \langle Q(\tau)\rangle ,$$

and

$$t = \int_0^\tau \frac{dt'}{\langle Q(t')\rangle} . \quad (25)$$

Equation (25) calculates the relation between t and τ from $\langle Q(t')\rangle$ which has itself already been calculated in Sec. IIC. From this relation, $\langle Q(t)\rangle_{\text{comp}}$ is obtained using (24). Figure 2 shows the compensated decay curves for the same parameters as were used for the case of Fig. 1 when N_d and N_a were unequal. Figure 3 shows a detailed comparison of curves for one concentration for the two cases. As is expected, at short times the exact compensation does not matter. At intermediate times, the decreased hole concentration decreases the recombination rate of an electron, so the exactly compensated curve falls below the partially compensated one once sufficient time has elapsed for about half of the carriers to recombine. For long times, the exactly compensated curves fall above the partially compensated ones because the recombination which did not take place at intermediate times finally occurs. Here, the compensated curves decay as t^{-2}.

The Hartree solution to the *model* problem is never expected to be particularly good in the interesting case

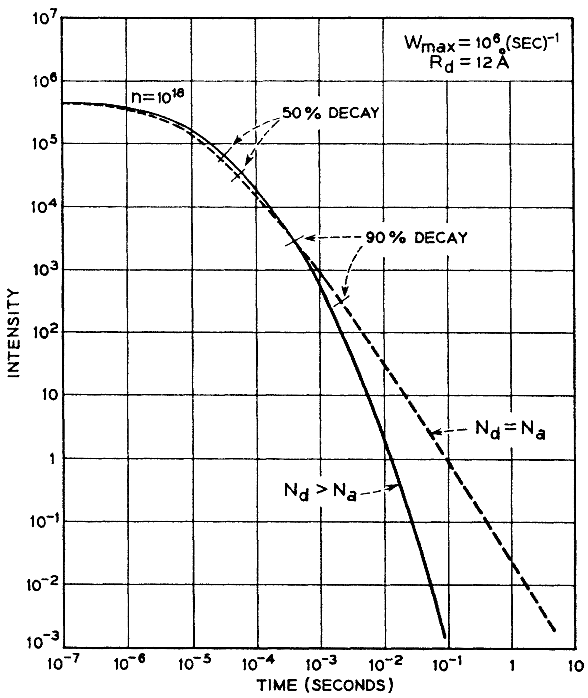

FIG. 3. A comparison of the theoretical decay curves for the exactly compensated and partially compensated cases.

of long times and low concentrations. Exact or nearly exact compensation, however, introduce the possibility of a new physical effect, namely the hopping of electrons and/or holes from one impurity to another when the sample has partially decayed. The effect of such hopping is to tend to maintain the different $\langle M_j \rangle_{av}$ at the same average value (at least for sites on which the energies are within kT). If the hopping is rapid compared to the rate of the optical processes, as it must be for long times, $\langle M_j \rangle_{av}$ will have no fluctuations, and the Hartree average would then be correct. Since in this limit hopping is the dominant factor, Eqs. (23) to (25) are identical to those given by Hoogenstraaten.[2]

The t^{-2} behavior of the Hartree solution for long times is the result of the redistribution of electrons and holes (implicit in the Hartree treatment) leading to bimolecular recombination. Additional complications in the presence of exact compensation include the effect of stray Coulomb fields due to other impurities on wave functions and energies. Neither the decay rate nor the decay energy of a pair is then a two-body problem.

In this paper we do not report on an experimental study of exactly compensated crystals.

F. Calculation of the Total Light Decay for Partially Saturated Systems. Donor or Acceptor in Excess

The time decay for systems in which the number of acceptors is much less than the number of donors, but for which the system is only partially pumped up at $t=0$ (i.e., some donors and acceptors are still ionized at $t=0$), may differ in two ways from the saturated case. First, there may exist at $t=0$ configurations in which a hole on an acceptor has some near-neighbor donor ionized. This acceptor will have an abnormal time decay. Secondly, a dependence of capture cross section on neighbor locations can provide a mechanism for selectively populating acceptors which have abnormally distant (or abnormally close) nearest neighbors.

The first situation can be treated in detail if it is assumed that donors and acceptors are populated at random. In the limit of very weak pumping, approximately one-third of the trapped holes have all surrounding donors neutral, one-third have one ionized donor nearby, and one-third have two (or more) ionized donors nearby. The light from those configurations having a nearest neighbor vacant has a much weaker intensity and slower decay for small times than that from saturated pairs, so the shape of the short-term time decay is similar to the saturated case. Experimentally, this is *not* the case—experimentally, in the limit of weak pumping the shape of the long-term time decay is the same as in the saturated case, while the short-term time decay is radically different for the two cases. One concludes that this effect is not important and that capture cross-section effects must be important in understanding the unsaturated time decay.

Capture cross section can best be looked at by beginning with a saturated pair which decays. The acceptor is left ionized, and a donor, typically the nearest neighbor, is also left ionized. The capture cross section of this ionized donor-acceptor pair for a hole (or electron) during the next excitation pulse is likely to be a strong function of separation. For large separations, the capture cross section will be that of the capture cross section of an isolated ionized acceptor (or donor), and, as has been shown by Lax,[14] will be very large. For small separations, the pair appears neutral, and will have a much smaller cross section. The form of the capture cross section for ionized pairs having a separation r will be taken to be

$$\sigma(r) = Ar^z. \qquad (26)$$

On intuitive grounds, one might expect the capture to be very efficient by Lax's Coulomb mechanism for impact parameters less than r, but negligible for impact parameters greater than r. Such intuition results in the value $z=2$. (No difficulty results from $r \to \infty$, for such nearest-neighbor pairs are present in vanishingly small numbers.) Once one carrier is captured, the center is charged, and the other carrier should be very quickly captured by Lax's process. The recombination process is therefore dominated by monomolecular kinetics, and all decays are expected to take place from saturated centers regardless of the level of excitation.

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[14] M. Lax, J. Phys. Chem. Solids 8, 66 (1959).

Let M be the integrated flux (particles/cm^2) incident on each center in the excitation process. If a center of separation r_c has a capture cross section $\sigma(r_c)$, the fraction of such centers pumped up by the flux M is

$$f(r_c,M)=1-\exp[-\sigma(r_c)M]. \quad (27)$$

The mean occupation $\langle Q(r_c,t)\rangle$ for a donor state having a *nearest* neighbor at r_c, averaged over all configurations of other neighbors, can be found by arguments similar to those already described, and is

$$\langle Q(r_c,t)\rangle=\exp\left\{\left[4\pi n\int_{r_c}^{\infty}\{\exp[-W(r)t]-1\}r^2dr\right]-W(r_c)t\right\}. \quad (28)$$

The time dependence of the total occupation is obtained by summing over all r_c weighted by their probability and is

$$\langle Q(M,t)\rangle_{\text{total}}=\int_0^{\infty}\langle Q(r_c,t)\rangle f(r_c,M)\times\left\{4\pi r^2 n\exp\left(-\frac{4\pi}{3}r^3n\right)\right\}dr. \quad (29)$$

The time decay of the intensity is

$$-(d/dt)\langle Q(M,t\rangle=J(M,t). \quad (30)$$

The numerical calculations from these equations are presented and discussed with the appropriate experimental data in Sec. IVB and in Figs. 8 and 9.

The relation between the integrated flux M and the energy of the exciting pulse depends upon the efficiency of pair emission in the crystal. If the efficiency is low, and many other traps are present, then the other traps will dominate the lifetime of the free carriers and will control M. For a carrier lifetime independent of carrier concentration, M would be proportional to I in this case of low efficiency. For a carrier lifetime controlled by capture at donor-acceptor pairs, M will depend nonlinearly on the total density n_i of bombardment-created electron-hole pairs. In this case when $n_i=n_t$, (n_t is the total number density of donor-acceptor pairs), all pairs have saturated, and M is infinite. M is large for finite n_i because the last few carriers see very few vacant donor-acceptor pairs and so have very long capture times. The exact dependence of M on n_i depends on the exponent (z) in (26). For the particularly simple case $z=3$,

$$M=(4\pi/3A)n[n_i/(n_t-n_i)], \quad (31)$$

where, as before, n is the majority defect concentration. For other values of z a much more complicated expression is obtained. The expressions are qualitatively similar, however, since all have M linear in n_i for small n_i and $M\rightarrow\infty$ for $n_i\rightarrow n_t$. The quantitative differences for different z as $n_i\rightarrow N$ have only a small effect on (27), which saturates rapidly in this region. All these results have of course presumed a uniform excitation density.

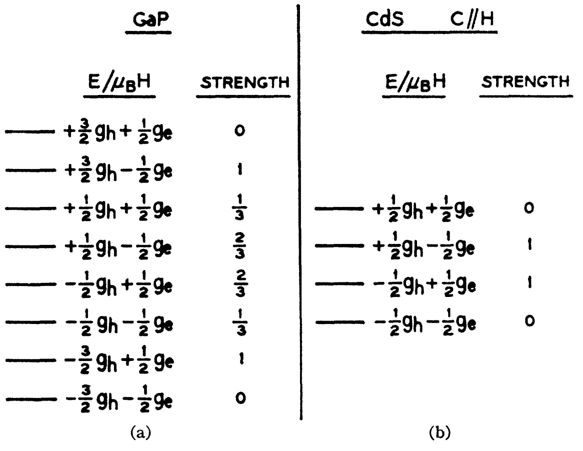

FIG. 4. A schematic diagram of the energy levels of the excited state of a donor-acceptor pair in a magnetic field for (a) GaP and (b) CdS, (the ordering of the levels depends on the relative values of g_e and g_h and are not necessarily correct). The relative values of the strengths of the optical transitions to the $J=0$ ground state are also given.

It might be noted that the decrease in capture cross section with decreasing separation leads at low light levels to a decrease in fluorescent efficiency if the minority component of concentration is held constant and the majority component increased. Optimization of efficiency of pair luminescence will require equal donor and acceptor concentrations.

G. The Effect of a Magnetic Field on $W_{\max}$

At low temperatures and high magnetic fields, the electron and hole will thermalize between Zeeman sublevels which arise from the electron and hole spins. The Zeeman sublevels and relative optical strengths to the ground state are shown in Figs. 4(a) and 4(b), for GaP and CdS, respectively. In each case, the lowest energy spin state corresponds to a $J_z=2$ state having no allowed optical transition to the ground state in any polarization. As a result, $W_{\max}$ decreases in large magnetic fields at low temperatures if the system can thermalize between the spin states before decay. If one writes

$$W_{\max}(H/T)=W_{\max}f(x), \quad (32)$$

where $x=\mu_BH/kT$, $f(x)$ is given by

$$f(x)=\frac{2\cosh\frac{1}{2}(g_e-g_h)x}{\cosh\frac{1}{2}(g_e-g_h)x+\cosh\frac{1}{2}(g_e+g_h)x} \quad (33)$$

in CdS, and by

$$f(x)=\frac{2\cosh\frac{1}{2}x(3g_h-g_e)+\frac{2}{3}\cosh\frac{1}{2}x(g_h+g_e)+\frac{4}{3}\cosh\frac{1}{2}x(g_h-g_e)}{\cosh\frac{1}{2}x(3g_h+g_e)+\cosh\frac{1}{2}x(3g_h-g_e)+\cosh\frac{1}{2}x(g_h+g_e)+\cosh\frac{1}{2}x(g_h-g_e)} \quad (34)$$

in GaP. In both cases, g_e and g_h are the g values of electron and hole, respectively; μ_B is the Bohr magneton. In CdS the magnetic field is assumed parallel to the c axis. For $H \perp c$ in CdS, g_h vanishes, and no effect of a magnetic field is expected. The case of CdS is conceptually simpler, for no angular redistribution of emitted radiation is induced by the magnetic field. In GaP, in addition to the alteration of $W_{\max}$ by the magnetic field, there is also an angular redistribution of the emitted light. At magnetic fields and temperatures available, this effect is quite small when the sample is viewed perpendicular to the magnetic field, never exceeding 10%, while the change in $W_{\max}$ is a factor of two or more.

III. EXPERIMENTAL

A. Crystals

In order to see green pair radiation in GaP the crystals should be grown from Ga solution. If the crystals are grown in quartz tubes without taking special precautions concerning the raw material purity, they usually show the Si-S type I_A pair spectrum. The crystals of GaP used in this investigation were grown by Trumbore using this method. In order to produce heavier sulphur doping, small quantities of Ga_2S_3 were added. Crystal M78 for which many results are quoted was nominally undoped but showed the Si-S pair spectrum. The crystals grow as irregular platelets, and for Hall measurements, and in order to provide a flat surface through which thermal contact could be made to a cold surface, the crystals were polished and sometimes cut into circles. Hall measurements were made by Montgomery[15] using the four-point van der Pauw method, the contacts being Au-Sn alloyed dots. The crystals were n type and analysis of the Hall curves indicated that the donor concentration (sulphur) exceeded the acceptor (silicon) concentration by about 10 to 1. However, anomalies in the Hall effect and in the spectra to be described below, indicated that other impurities were present in the crystals.

B. Excitation of Photoluminescence

For some work it was desirable to have the crystals immersed in liquid hydrogen or helium which was contained in a glass Dewar. Excitation was then produced by blue and ultraviolet light. For continuous excitation two high-pressure mercury arcs were focused onto the crystals through Corning 7-59 filters; a Corning 3-70 filter was used at the entrance slit of the spectrometer. Spectra were taken using a 1P28 photomultiplier in conjunction with a 2-m Bausch and Lomb spectrometer. Most of the work involved studying the decay of the photoluminescence after an abrupt burst of excitation was provided either by light from an FX12 Xenon flash lamp, or by a burst of electrons from a Van de Graaff accelerator. The filtered radiation from the flash lamp was focused onto the crystal by an $f/1$ lens. The lamp was energized by discharging 0.025 μF charged to 8000 V through an E.G.G. matching transformer. The discharge was controlled by a thyratron driven by a low-frequency oscillator. The afterglow of the flash lamp and electrical transients prevented useful measurements before about 25 μsec after the excitation. The light from the flash lamp is absorbed within about 10^{-4} cm of the surface. In a single flash, more hole electron pairs are made within this distance of the surface than there are donors and acceptors. Consequently, all of the impurities will be momentarily neutralized, (saturated); the excess holes and electrons may recombine by other mechanisms or may diffuse further into the crystal. It follows that if it is desired to look at the light from an incompletely saturated system this method of excitation is not very useful, since such a small volume of the crystal will be excited by the attenuated radiation that the subsequently emitted light will be very feeble. The method, however, requires only simple apparatus, and can be used for samples immersed in a refrigerant, so that if low temperatures, such as 1.6°K, are desired the method is a useful one. Thus the method was used for the low-temperature experiments in a magnetic field, in which the crystals were held in the Dewar tip between the pole pieces of a magnet which produced a field of 31 kG.

The Van de Graaff accelerator, made by High Voltage Engineering, had been modified to produce 9-μsec or 30-nsec pulses of electrons at currents up to several mA. The 9-μsec pulse had a cutoff time of 0.5 μsec. The accelerator was operated at 350 keV, and total doses received by a sample were about 2×10^{15} electrons/cm^2. Under these conditions little or no radiation damage was produced in the crystals, as judged by very small changes in the fluorescent efficiency before and after a series of experiments. There was some spatial jitter in the beam the effects of which were minimized by passing the beam through a 0.001-in. thick foil of Be. The crystal was placed beyond this foil so that a beam current of 1 mA produced a current density at the crystal of about 2 mA/cm^2. The range of electrons in GaP has been estimated from theoretical curves[16,17] of elements close to gallium and phosphorus. The estimates show that the range of a 350-keV electron in GaP is about 0.3 mm. Our samples were 0.15-mm thick and were easily penetrated by the electrons. The energy loss in this amount of GaP would be approximately 100 keV. If it is assumed that three times the band gap energy is necessary to make a hole electron pair, an energy of 7 eV is required for GaP. Using this we find

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[15] H. C. Montgomery and W. L. Feldmann, J. Appl. Phys. (to be published).

[16] A. T. Nelms, Nat. Bur. Std. Circ. 577, 1958.

[17] M. J. Berger and S. M. Seltzer, National Aeronautics and Space Administration Report No. NASA SP-3012 (Office of Technical Services, Department of Commerce, Washington, D. C., 1964).

that a 9 μsec, 1.7 mA, 350-keV pulse as used here will produce 2×10^{17} hole electron pairs/cc. Thus it is reasonable to suppose that crystals doped to this level with the minority impurity may be saturated by the 9-μsec pulse. That this indeed does happen is shown by more direct evidence described below. Since a comparatively large volume of the crystal is excited the light is bright, and if the current is diminished, or the pulse length shortened this volume is not decreased. Consequently, the emission from partially saturated systems will be reasonably intense and its decay can be followed without great difficulty.

The crystal was held in the vacuum space of the Van de Graaff accelerator and was clipped to a cold copper finger with fine silver dust between the GaP and the copper. A thermocouple soldered to the crystal indicated that the temperature was within 4°K of the temperature of liquid hydrogen (20.5°K). Around the crystal were two copper heat shields each attached to the liquid-hydrogen reservoir. Both had small holes for the incoming electron beam and at right angles larger holes for the outgoing light. The outer of these holes was covered with a window cooled by contact with the radiation shield. Strong fluorescence from this cold window was excited by scattered electrons. Several window materials were tried to minimize this effect, (single crystal quartz, sapphire, suprasil quartz), but pyrex was found to give the least interference. The problem of this radiation was negligible when spectra were being taken, because the radiation from the window occurred over a wide spectral region. For the total light experiments in which all the pair radiation was observed, two interference filters were used which passed light between 2.1 and 2.5 eV, thereby cutting out much of the radiation from the window but passing the pair radiation. The light passed from the vacuum region through a lens, which formed the vacuum seal and which rendered the light parallel. The light then passed through a tunnel in a large lead castle which surrounded the target area. This light could fall on a photomultiplier, (RCA 6655), directly for the total light experiment, or could be focused onto the slit of a Bausch and Lomb 500-mm monochromator and then onto a photomultiplier if spectra were to be taken.

C. Observation of Spectra as a Function of Time

Total light decay curves were taken in which all the pair radiation is collected and its decay of intensity is followed as a function of time after the end of the pulse excitation. In addition, complete spectra were taken at certain times after the excitation. In both cases the data were read point by point from an oscilloscope. At each point several pulses were observed and an average struck. Care was taken to leave sufficient interval between pulses so that the readings were not a function of repetition rate. This could happen in the Van de Graaff experiments in which partially saturated systems were being examined, for if decay were not complete before the next flash arrived, the degree of saturation would be greater for the second than for the first flash. In the flash lamp experiments although saturation is presumably always obtained, a rapid flash rate can produce excitation of a greater volume of the crystal by diffusion of the excess carriers. As the time of observation was increased the *R* and *C* in the photomultiplier output circuit were progressively increased. Because the decay very approximately obeyed a t^{-1} law, measurements could be made over many factors of 10 in time without large changes in the signal-to-noise ratio.

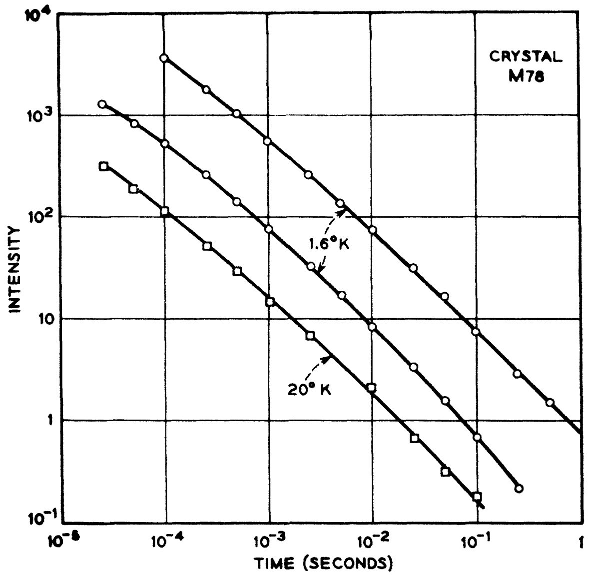

FIG. 5. The total light decay curves of GaP crystal M78 at 20° and 1.6°K. Two flashlight intensities were used at 1.6°K. The displacement of the 20 and 1.6°K curves is of no significance (see text).

IV. RESULTS AND COMPARISON WITH THEORY

A. Temperature Dependence

In the model considered to explain the results it is assumed that once the holes and electrons are trapped, they remain trapped, so that for low temperatures and for finite times the decay should be independent of temperature. This should be true for the shape of the decay curve, and also for its intensity provided the carriers are trapped with an efficiency that is also independent of temperature. Between 20 and 1.6°K within the experimental accuracy this has been found to be so. Figure 5 shows data taken on a crystal at 1.6 and 20°K excited with the flash lamp. The displacement between the two lowest curves arises from different geometrical factors for these two experiments. Other experiments have shown that for most crystal the intensities of the curves are very similar at 20 and 1.6°K. The highest lying curve in Fig. 5 shows the

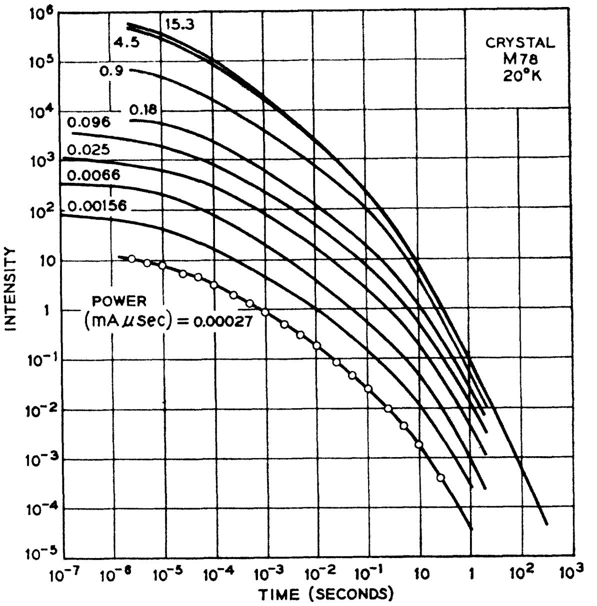

FIG. 6. A series of total light decay curves for GaP crystal M78 excited by pulses of different power from the Van de Graaff machine. The electron energy is 350 keV. The pulse powers are indicated and the top two curves show that saturation has been attained. The experimental points have been shown for only one curve.

results at 1.6°K if the excitation intensity is increased. All three curves have very similar shapes showing that over this temperature and intensity range the shapes of the curves are independent of temperature and excitation intensity. The temperature independence could not be understood if thermal detrapping effects were important in controlling the kinetics of the decay. The independence of shape on excitation intensity indicates that the flash lamp does produce an initially saturated system as discussed in the next section.

B. Analysis of the Total Light Decay. Capture Cross Section Effects

A crystal was chosen which gave decay curves and decay spectra that did not display obvious anomalies due to faulty doping (see Sec. IVD). In order to obtain the data over as wide a time range as possible, and particularly to observe the early stages of the decay, the Van de Graaff accelerator was much more suitable than the flash lamp. The Van de Graaff could only be used with the crystal at 20°K, but as the previous section showed, there is no need with silicon and sulphur impurities to go to lower temperatures.

Figure 6 shows a set of total light decay curves for crystal M78. The curves were taken for different beam currents and pulse durations so that the pulse power is varied and is marked on each curve. The most intense pulses were able to saturate the pair emission. This is shown by the virtual coincidence of the two highest curves, even though one has more than three times the input power of the other. At much lower power levels the intensity level of the curves varies linearly with the input power. Saturation is also demonstrated by the oscillograms shown in Fig. 7. These traces show the light output from the crystal during and immediately after the pulse, and correspond to some of the pulse intensities shown in the previous figure. At low pulse intensities the light builds up linearly as the pairs are populated, for the decay during the pulse is negligible compared to the excitation rate. At the high intensities the pairs quickly become saturated and the light output follows the pulse. Figure 10 shows the spectrum during such a pulse, (the curve marked 0 secs), from which it is seen that some of the light during this time comes

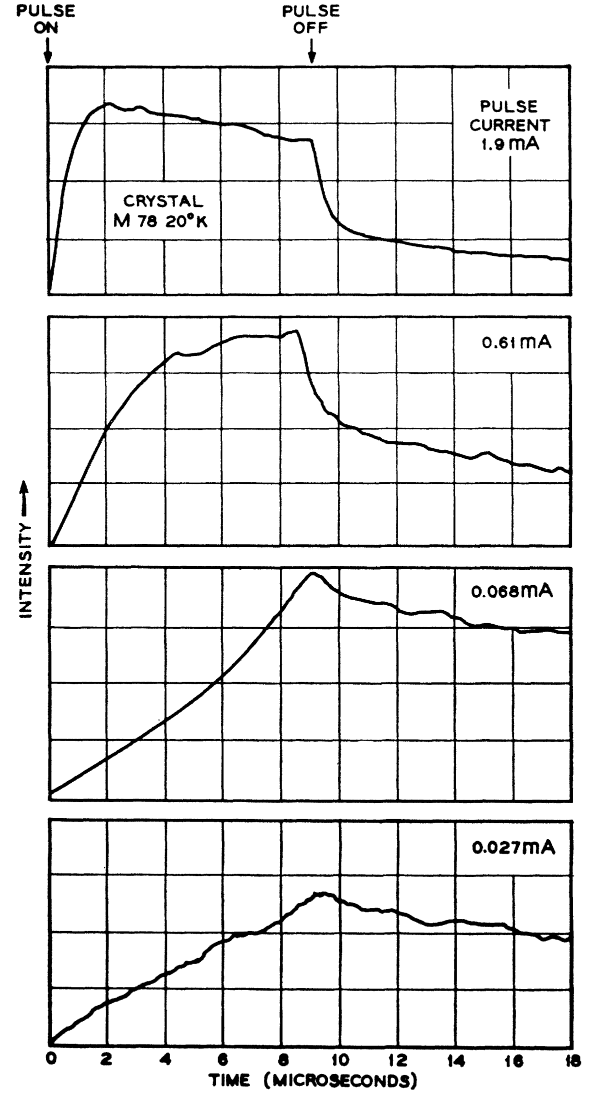

FIG. 7. The light output during and immediately after the Van de Graaff pulse for different pulse powers. At low powers the pair emission occurs with a slow decay. As the pairs become saturated faster bound-exciton emission becomes important.

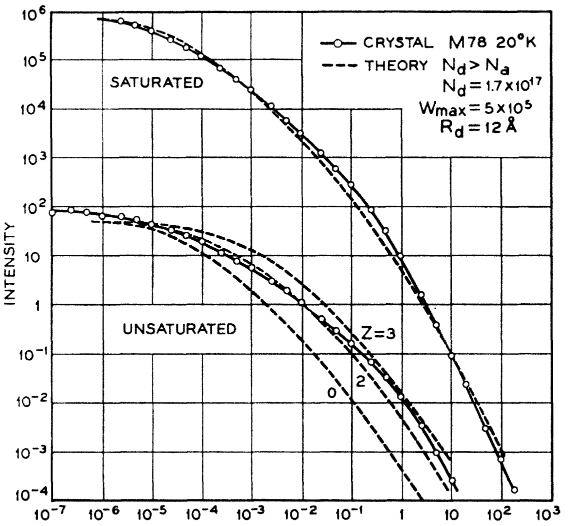

FIG. 8. A comparison of theory and experiment for GaP crystal M78 for which Hall measurements gave $N_d = 1.7\times 10^{17}$ and $N_d > N_a$. The saturated curve is fitted with the $W_{\max}$ and R_d values indicated. The low level unsaturated curve is compared with theory using the same values of $W_{\max}$ and R_d and different values of z, the exponent in Eq. (27).

from bound excitons, (such as the lines marked *A* and *C*), which have a short lifetime compared to the 9-μsec pulse. The fast decay of these lines at the end of the pulse indicates that free hole electron pairs are rapidly trapped and will not interfere with subsequent decay kinetics. It was shown in Sec. IIIB that it is quantitatively reasonable that the most intense pulses should saturate samples such as M78. That this is observed to be the case indicates that most of the electrons and holes are trapped by radiative centers. Further confirmation of this is provided by observations of Maeda[18] in which fluorescent quantum efficiencies near unity have been reported for the low-temperature pair emission of suitably doped GaP.

The results of Fig. 6 indicate that there is a considerable change of shape of the total light decay curves between the saturated and unsaturated conditions. As the pulse power is decreased the initial decay is delayed so that the curves become flatter. At very low powers the curves are parallel and have a constant shape. If the same crystal is excited by the strongly absorbed light from the flash lamp the total light decay curve has the same shape as the saturated Van de Graaff curve. However, increasing or decreasing the flash intensity does increase or decrease the intensity of the decay curve without altering its shape (see Fig. 5). This is strong evidence that as the flash intensity is increased there is greater penetration of the holes and electrons into the bulk of the crystal.

The Hall effect measurements performed by Montgomery indicate that for crystal M78 the concentration of donors, N_d, is 1.7×10^{17}/cc and the concentration of acceptors, N_a, is less than 3×10^{16}/cc. In comparing the decay results with theory it is therefore appropriate to use the approximation that one of the impurities is in greater concentration than the other. The procedure adopted was to make the best over-all fit of the saturated total light curve to one of the calculated curves of Fig. 1. Figure 8 shows this fit. In making this match there is freedom in the vertical scale since this relates to the over-all quantum efficiency, which, for heavily doped crystals, may be less than unity. The shift of the horizontal scale corresponds to changes in the value of $W_{\max}$, and the particular curve chosen fixes the value of the parameter $N_dR_d^3$. Knowing N_d, R_d may be obtained. In this way the following values were deduced: $W_{\max} = 5\times 10^5$ sec^{-1}, $R_d = 12$ Å. The fit is reasonable over many factors of 10 in time and intensity but it is not perfect and so these parameters are not precisely defined. In an earlier report[6] using data taken with the flash lamp rather than with the Van de Graaff machine, with the result that the initial part of the curve was unobserved, $W_{\max}$ was estimated to be 10^6 sec^{-1}, and R_d to be 8 Å. It is considered that in view of the limited data then available these values are in reasonable agreement with the ones quoted above.

Figure 8 also shows the limiting decay curve for low-intensity pumping. With this curve are presented the limiting low-intensity curves calculated for the total light decay of nonsaturated systems, using the capture cross-section effect as described in Sec. IIF. Three curves are shown for values of z, the exponent in Eq. (26), equal to 0, 2, and 3 (the curve of $z=0$ being the normal saturated curve). The other parameters are

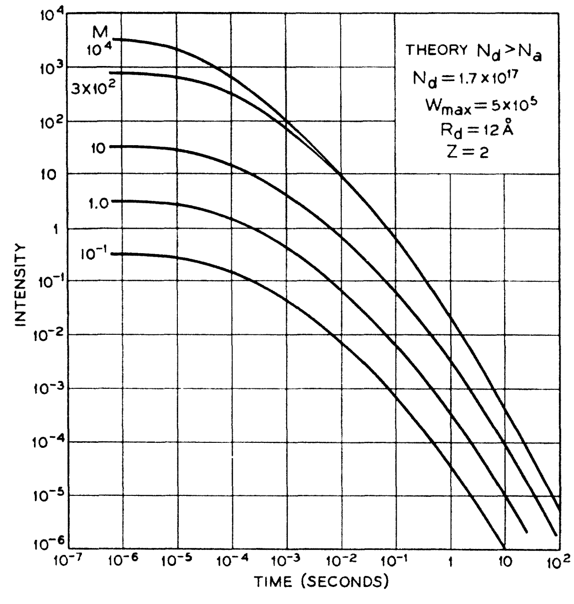

FIG. 9. Theoretical curves of the total light decay using the parameters appropriate for crystal M78. It is assumed that $z=2$. This figure is to be compared to Fig. 6.

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[18] K. Maeda, J. Phys. Chem. Solids (to be published).

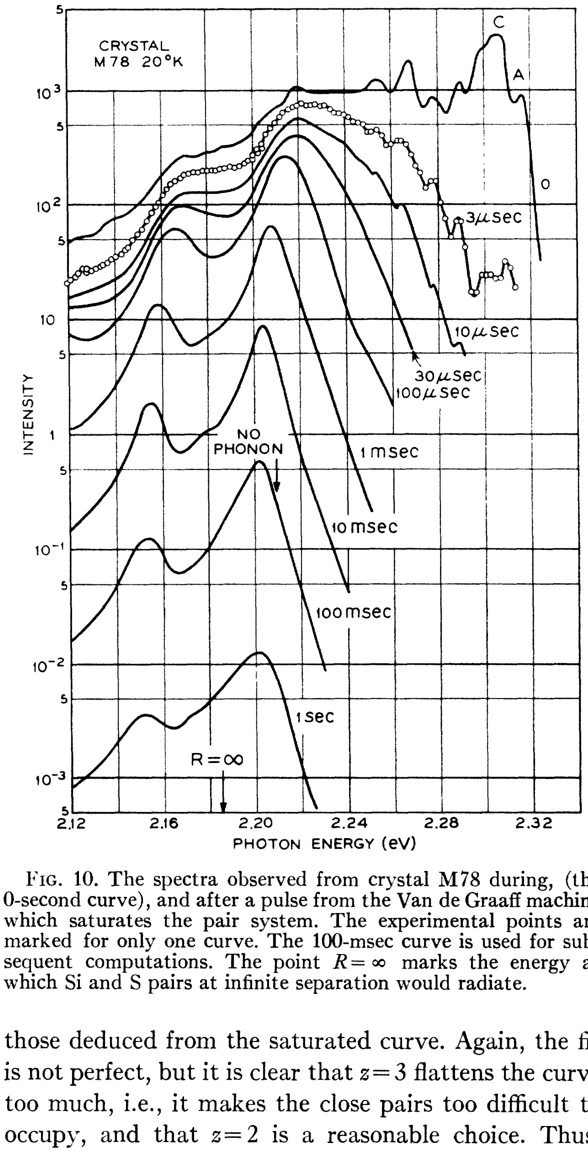

FIG. 10. The spectra observed from crystal M78 during, (the 0-second curve), and after a pulse from the Van de Graaff machine which saturates the pair system. The experimental points are marked for only one curve. The 100-msec curve is used for subsequent computations. The point $R=\infty$ marks the energy at which Si and S pairs at infinite separation would radiate.

those deduced from the saturated curve. Again, the fit is not perfect, but it is clear that $z=3$ flattens the curve too much, i.e., it makes the close pairs too difficult to occupy, and that $z=2$ is a reasonable choice. Thus, from the shape of the low-intensity curves, information is derived about the relation between capture cross section and pair separation.

Finally, a set of curves, Fig. 9, have been calculated using the parameters deduced so far which show the expected decay curves as the degree of saturation is decreased. The parameter which changes from one curve to another is M which, as explained in Sec. IIF, is not simply related to the input pulse power. It is clear from a comparison of this figure with that showing the experimental data that there is approximate agreement between theory and experiment concerning the change of shape with the change of intensity of the emission. Thus, for both theory and experiment the curves have achieved an approximately constant shape when the initial intensity has fallen by about a factor of 100.

C. Analysis of Spectral Decay

Using the high power pulse, so that the system was saturated, the spectra were taken at different times during the decay. Figure 10 shows these spectra for crystal M78. Included in this figure is the spectral output taken while the pulse is on (the 0 second curve). This curve shows structure which includes bound exciton decay, (the bands marked A and C) as is expected for vigorous continuous excitation. In addition, the individual close-spaced pair lines may be responsible for some of the structure. This structure was observed with the 30-nsec pulse and found to have lifetimes of 10^{-8} sec or less. The broad pair emission spectra are remarkable because they change shape as time passes. At early times there is a marked broadening on the high-energy side, but this declines and the spectra assume an approximately constant shape and move to lower energies as time increases. At the one-second curve, there appears to be some distortion of the spectrum resulting in a less well-defined valley between the peaks;

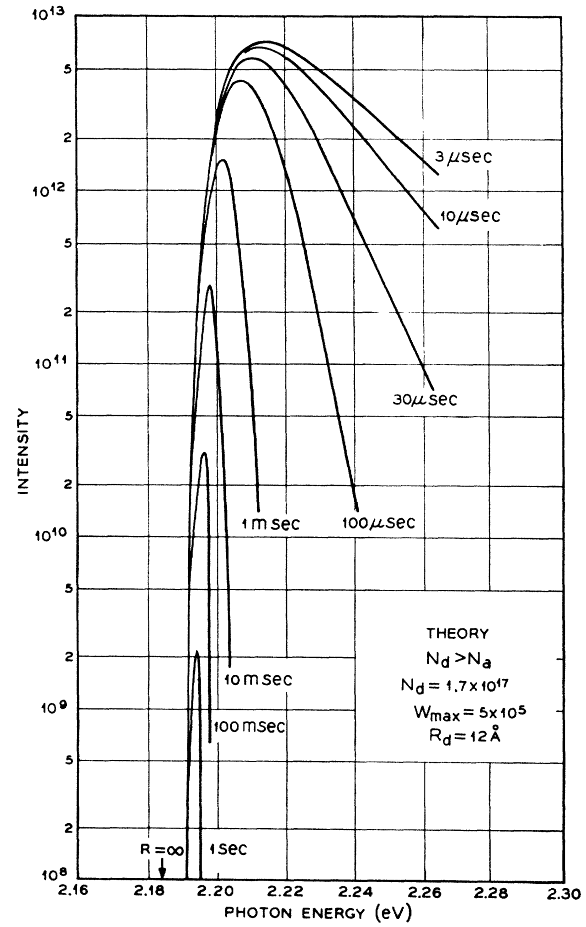

FIG. 11. Theoretical curve for the spectra from the Si-S pair system in GaP assuming that a pair of separation r radiates *only* at the photon energy given by Eq. (1). The parameters used are indicated.

this is probably a weak example of the anomalies discussed below. The two peaks are separated by about 0.05 eV which is equal to the longitudinal-optic (LO) phonon energy; the lower energy peak is clearly a phonon replica of the high energy peak, and indeed it has been shown[4] that several replicas can be seen at successively lower energies. The filling in of the valley between the peaks at early times is caused by the phonon repeat of the broadening on the high-energy side of the first peak.

These results can be understood in terms of emission from pairs. The close pairs have a shorter lifetime than more distant pairs, and they radiate at a higher photon energy because of the Coulombic interactions described in Eq. (1). Thus the early emission occurs at higher energies than the later emission. The marked "pair" broadening at early times arises in the following way. At any particular time, pairs with a certain range of lifetimes are being observed; since the lifetimes vary exponentially with the separation between the members of a pair, a certain range of lifetime corresponds to a certain increment of separation independent of the actual value of the separation. At short separations this increment results in a substantial energy change, but at larger separations it does not. Hence significant pair broadening is seen at early times but not at late times.

So far it has been implied that a particular pair radiates only at the "no-phonon" energy given by Eq. (1). Clearly this is not so, for if it were there would be no radiation at energies below that corresponding to infinite pair separation, which is 2.1866 eV for Si-S pairs at 20°K and is marked by an arrow in Fig. 10. It is expected that at very low temperatures the emission from a pair will consist of a sharp no-phonon line and at lower energies phonon wings arising not only from LO phonons, but also from acoustic phonons which will produce wings over a range of energies from the no-phonon line. Examples of such wings on no-phonon lines are provided by the decay of excitons bound to point defects where pair-broadening effects do not obscure the no-phonon line.[19,20] The basic line shape might therefore resemble the spectrum taken at long times when the pair broadening is minimized, although it is hardly to be expected that the very sharp no-phonon line will become apparent. The limiting curves are found to vary from one crystal to another; contrast for instance the long time curves of Fig. 10 and Figs. 16 and 18. The residual broadening does not therefore arise only from phonon effects. Other possibilities are different chemical species which may give emission at different energies, and also electric fields in the crystal arising from charged centers. The effects of these fields are particularly severe on the distant pairs, for the ground state of the transition consists of a dipole with a large dipole moment, and this will have an energy strongly dependent on the presence of an electric field.[21] The procedure adopted is therefore to take the limiting curve of a crystal as being characteristic of that crystal alone.

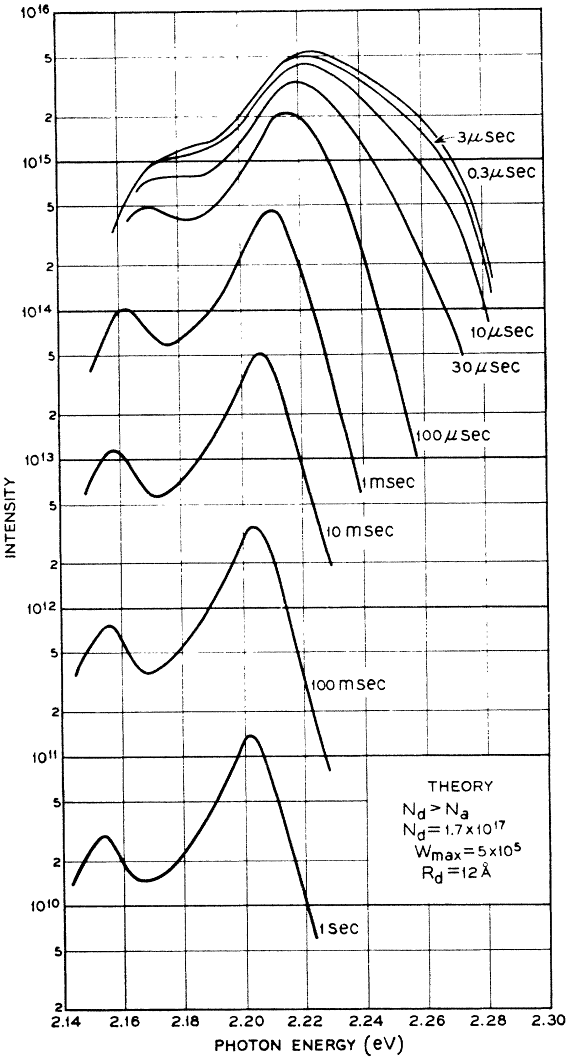

FIG. 12. Theoretical spectra for the parameters indicated. The curves are based on those of Fig. 11 with the additional assumption that the pairs radiate with a spectral line shape given by the 100 msec curve of Fig. 10.

In order to make a quantitative test of the theory the data of Fig. 10 have been considered in detail. Using the values of $W_{\max}$ and R_d deduced from the total light decay of crystal M78, together with the known parameters of Eq. (1) for Si-S pairs, the spectral output has been calculated as described in Sec. IID, assuming that the pairs radiate *only* at the no-phonon line. The results are shown in Fig. 11, in which the shift of the peak and its broadening at early times, both caused by the pair interaction, are clearly seen. The results of a complete

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

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

[21] K. Colbow, Phys. Rev. **139**, A274 (1965).

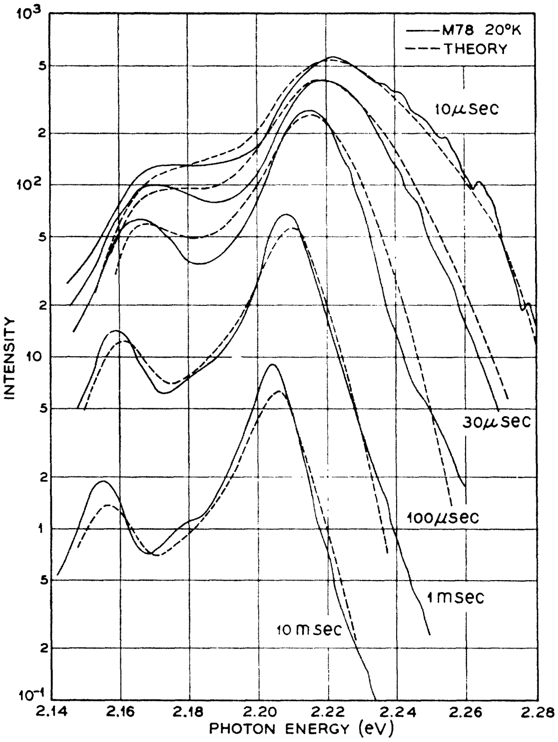

FIG. 13. A comparison of some of the experimental curves of Fig. 10 with the theoretical curves of Fig. 12.

synthesis of the spectra are shown in Fig. 12. In this synthesis the experimental spectrum at a time of 100 msec in Fig. 10 has been used to give the fundamental line shape. It is also necessary to decide at what point on this spectrum the zero-phonon energy is to be taken. This was done by choosing the point in such a way that the energy of the peak in the calculated spectrum at 100 msec, coincided with the observed peak at this time. This resulted in the no-phonon energy falling at an energy 0.007 eV above the peak in the spectrum (the point is marked by an arrow on the 100 msec curve of Fig. 10). This position is considered reasonable, for ideally the no-phonon line should lie at the highest energy point of the curve taken at 0°K. The actual temperature of 20°K and the various broadening mechanisms discussed above could produce some emission above the no-phonon line. It can be seen that there is quite good agreement between the observed and calculated spectra (Figs. 10 and 12). Figure 13 shows a detailed comparison of the theory and experiment for the early stages of the decay when pair broadening is important; in general, the agreement is good.

As a result of the variation of capture cross section with pair separation it is more difficult to populate the close pairs than the distant pairs, and unless the system is saturated the distant pairs will be preferentially occupied. It is the close pairs which are responsible for the pair broadening at early times, so that decay of a partially saturated system would be expected to show less broadening than a saturated system. Figure 14 illustrates this. It shows two spectra both taken at 10 μsec, one from the saturated crystal the other from the crystal after excitation with a much weaker pulse. To aid comparison the curves have been plotted next to each other, although the unsaturated curve is 8.6 times weaker than the saturated one. It can be seen that, as expected, the partially saturated crystal gives a sharper spectrum and one peaked at a lower energy than the saturated crystal.

D. Higher Concentrations and Deviations from Simple Decay

Several crystals of GaP have been studied. While they all gave results qualitatively similar to those just described, the results could not all be so simply compared to theory. An example is crystal M61 which was purposely doped with sulphur. Hall measurements indicated that this crystal had $N_d = 10^{18}$ and $N_a = 1.2 \times 10^{17}$. Photoluminscent spectra showed the presence of Si-S pairs. Figure 15 shows the saturated, total light decay of this crystal, and dotted in is a fit to a theoretical curve for $N_d = 10^{18}$, and the $W_{\max}$ and R_d values that were deduced for crystal M78. There is quite good agreement between the observed and calculated curves up to about 1 msec, but beyond this point the observed decay is much slower than expected. Figure 16 shows the corresponding spectra taken during the decay of the fluorescence. In the initial stages the spectra are quite normal, in that they are peaked at the expected energies and show pair broadening. However, the spectra at 10 and 100 msec are clearly abnormal, being peaked at too low photon energies. The time at which these anomalies become dominant coincides with the time at which the total light decay departs from the simple curve. It seems clear that in this crystal there is

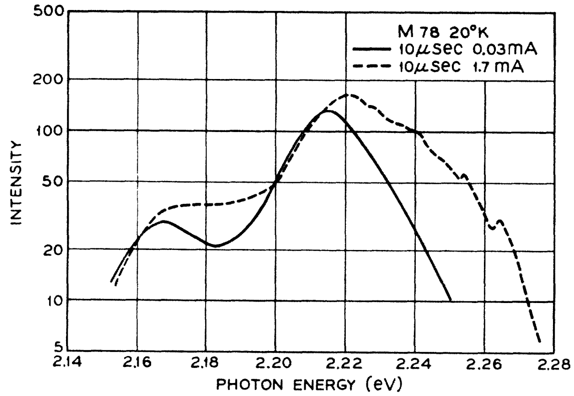

FIG. 14. Two spectra taken at 10 μsec. The solid line was for a pulse which only partially saturated the pairs, the dotted line for a pulse which completely saturated the pairs. The former curve is 8.6 times weaker than the latter, but they have been drawn together for ease of comparison.

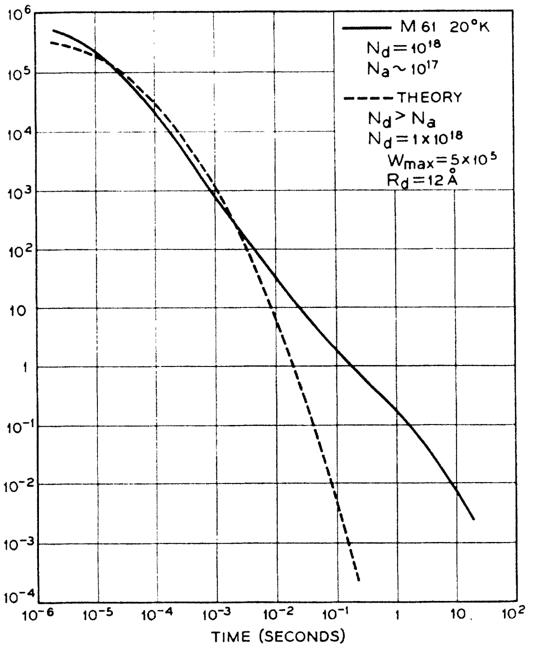

FIG. 15. Comparison of theory and experiment for the total light decay of a crystal of GaP more heavily doped than M78.

another impurity involved which gives a larger value to $(E_a + E_d)$, and a fluorescence that decays more slowly than the Si-S pairs. Initially, the intensity of this emission is negligible but as the Si-S pairs decay more rapidly, it becomes dominant at later times. (At 1 msec, calculations indicate that 92% of the Si-S pairs have decayed.) Presumably this impurity is a minority impurity, and so an acceptor in n-type material. Since it decays more slowly than Si it presumably causes the value of R_d to be less than that for Si and S pairs. In view of the fact that S always has the largest binding energy in the pairs, it is expected that the overlap, and so R_d, will be dominated by the acceptors. The unknown acceptor has a larger binding energy than Si (for the anomalous peak is at a lower energy than the Si-S peak), and this is consistent with a smaller R_d. Rather similar anomalies have been described by Gross and Nedzvetsky,[7,8] presumably also due to crystals which did not contain just one type of donor acceptor pair.

A still more concentrated crystal was M63 with $N_d = 4 \times 10^{18}$/cc and $N_a = 2.5 \times 10^{17}$/cc, as determined by Hall measurements. The total light decay curve is shown in Fig. 17 with the expected curve for 3×10^{18}/cc dotted in. Although the experimental curve is steeper than for the other crystals, particularly in the early stages, in the later stages it is not as steep as the theoretical curve. Figure 18 shows the spectra taken at different times for this crystal. At early times the Si-S pair emission is recognizable but at later times it has disappeared, and instead there is a peak which at 1 msec lies below the energy of Si-S pairs at infinite separation (2.1866 eV). In addition, there is a continous broad emission at longer wavelengths. All of the later radiation is therefore not connected with Si-S pairs; when there is deviation from the expected total light decay curve the Si-S radiation has disappeared. At this higher concentration the control of the chemistry of the crystal has been lost. Whether the deeper states arise from different impurities, or from aggregation of the concentrated impurities is not clear, but the continuous nature of the emission suggests the formation of a wide range of energy states which may ultimately form the nonradiative recombination centers responsible for concentration quenching.

Thus, crystals with higher donor concentrations do decay more rapidly as expected, but precise and complete quantitative agreement with the simple theory has not so far been achieved. However, when there is deviation from expectations examination of the spectra show clearly that emission processes other than the Si-S pair decay are present.

E. Similar Results with Cadmium Sulphide

A previous publication[6] has presented spectra as a function of time after flash excitation of CdS at 1.6°K.

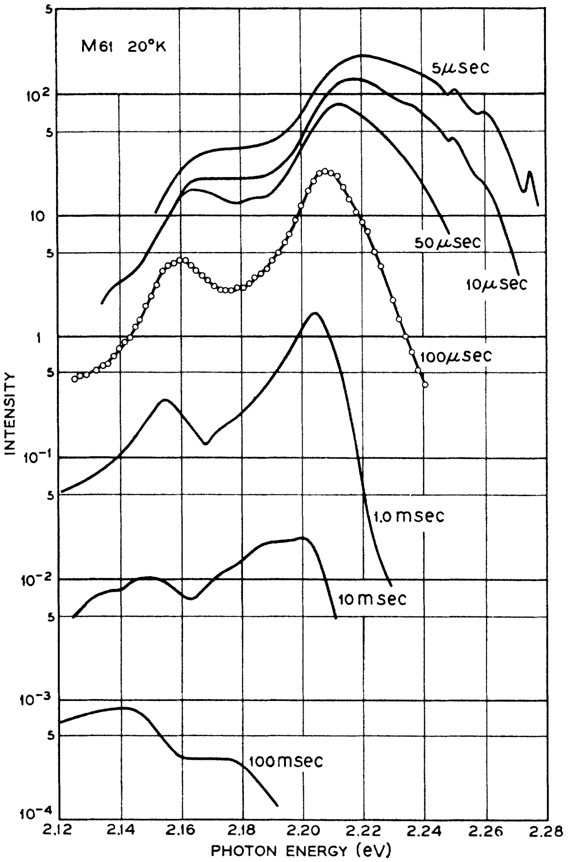

FIG. 16. The spectral output as a function of time after excitation with the Van de Graaff machine for the crystal used in Fig. 15. Notice the anomalous results after 1 msec. The experimental points are given for only one curve.

The fluorescent decay extended over many seconds, and consisted of the well-known green "edge" emission of CdS which falls about 0.18 eV below the band gap. The spectra shifted to longer wavelength as a function of time much as the GaP spectra, however spectral broadening was not seen at early times. The total light decay was also similar to GaP although it was not possible to see the initial flat part of the decay. Thus it is concluded that pair emission is occurring in CdS but that the values of $W_{\max}$ and R_d are such that saturation of the system was not observed. This may be partly because optical lifetimes will be rather short in CdS since it is a direct band gap material, and also because holes and electrons made close to the surface may diffuse rapidly into the crystal. The effects of a high magnetic field on the total light decay at 1.6°K were observed and further confirmed the view that pair emission was involved. Individual pair lines have not been seen in CdS, possibly because there was insufficiently vigorous continuous excitation.

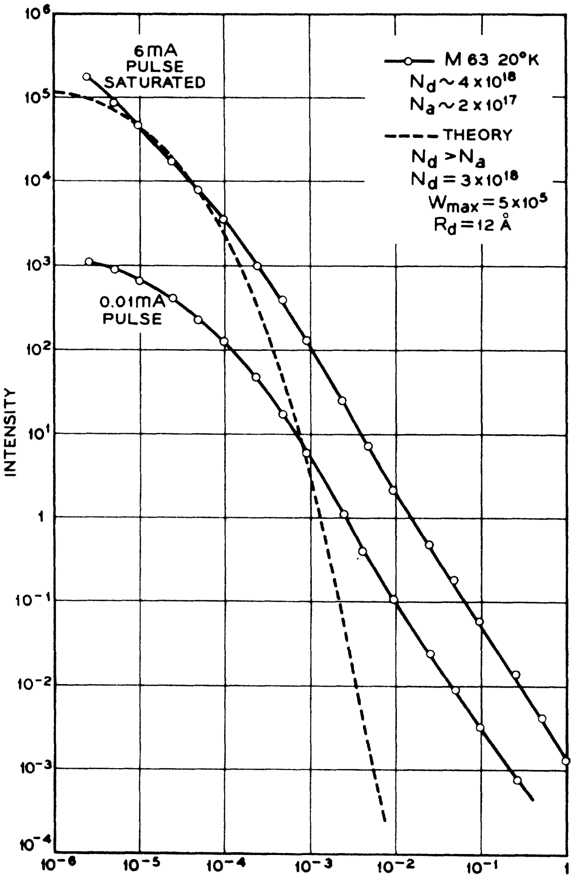

FIG. 17. The total light decay of a GaP crystal doped more heavily than M61. The saturated and partially saturated decay are shown, and the saturated curve is compared with the expected theoretical curve.

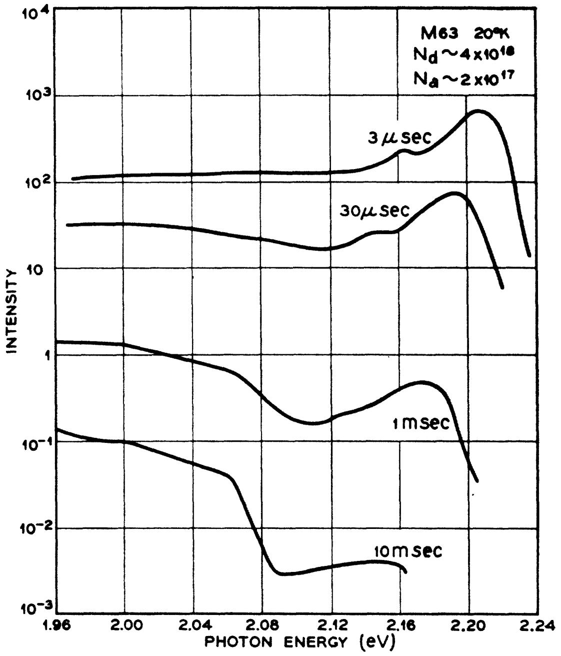

FIG. 18. The spectral decay of M63 which is seen to be highly anomalous.

F. The Effect of a Magnetic Field on the Rate of Decay

Section IIG showed that a magnetic field applied at low temperatures could reduce the decay rate of all the pairs by a constant factor $f(x)$. In Sec. IIC it is explained that this is expected to slide all decay curves on log-log plots downwards in intensity, and across in time by the same factor $f(x)$. Thus if on such a plot the zero-field decay has a slope of 45° the effect of a magnetic field is not expected to be detectable. For low-temperature measurements the crystal is immersed in liquid helium and so a flash lamp is used for excitation which limits the time range over which measurements are possible. For a number of the crystals used this available time range gave total light decay curves with slopes rather close to 45°, so that the magnetic effects were small. However, some suitable crystals of GaP were found and the results of the total light decay, and the decay at two different photon energies in the pair band are shown in Figs. 19(a) and 19(b). In all cases it can be seen that at a 45° slope the effect of a field disappears, and that for flatter curves the field diminishes the intensity and for steeper curves it enhances it in agreement with expectation. At 20°K decay curves of identical shape are observed but they are unaffected by the field. It is found that the value of $f(x)$ at 1.6°K and 31000 G is 0.55 ± 0.1, for all of the crystals examined. It is reasonable to assume that the g value of the electron on any normal donor will be approximately constant at 2.0.[22] Equation (34) then

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[22] Y. Yafet and D. G. Thomas, Phys. Rev. **131**, 2405 (1963).

gives a value of 0.53±0.12 for the g value of a hole on a silicon acceptor. At present there is no directly measured value of this quantity.

G. Spectra Produced by Continuous Excitation

In order to see the individual pair lines the crystals are excited continuously and a spectrum of the fluorescence is taken. The lines however only appear when the crystals have reasonably low donor and acceptor concentrations and when the crystals are being intensely excited. If the excitation intensity is diminished the lines disappear, and the remaining broad emission becomes narrower and moves to longer wavelengths. All of these phenomena are illustrated in Fig. 20, in which logarithmic spectra are shown for a lightly doped crystal, at different exciting intensities. At high intensities the pair lines are visible, but these disappear for the weaker exciting intensities.

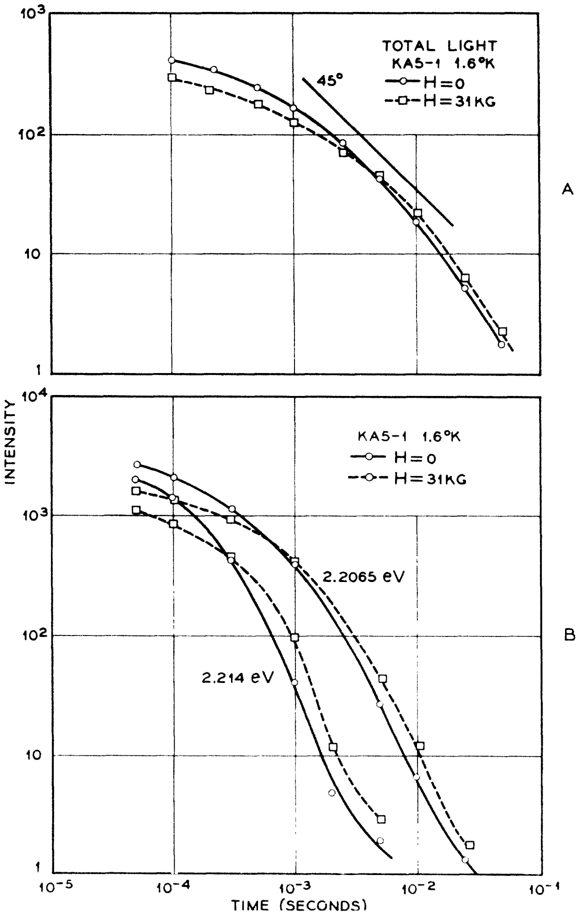

FIG. 19. The effect of a magnetic field at low temperatures on the decay of GaP crystal KA5-1. A shows the decay of the total light. B shows the decay at two different photon energies in the pair band.

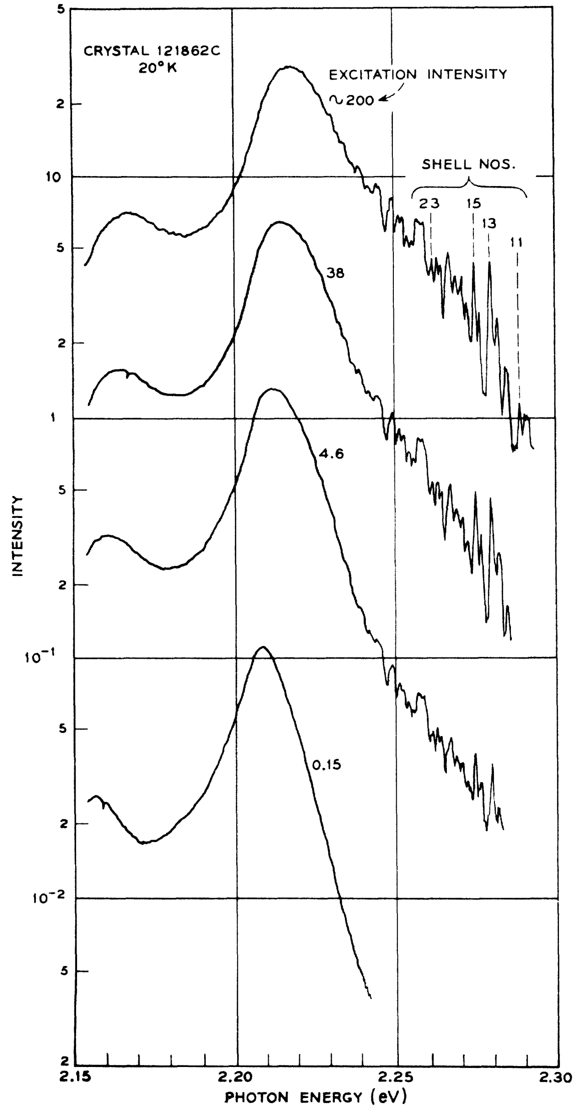

FIG. 20. Si-S pair spectra in GaP taken using continuous excitation at a series of different excitation intensities. At lower intensities the line spectra become relatively less intense. The shell numbers of certain pair lines have been marked.

It is likely that in order to see the individual pair lines in a system in which the donors and acceptors are arranged randomly, continuous intense pumping will be necessary. The reason is that only atypical close, isolated, pairs will show individual lines, for pairs with typical separations will not be isolated and will suffer from broadening effects. However, the closer pairs will be fewer in number and if observed in an experiment such as a flash experiment, in which every pair decays just once, they will have insignificant intensities compared to the typical pairs. Intense continuous excitation however accents the close pairs, for the distant pairs become saturated and the close pairs can then decay many times for every time a distant pair decays, since the close pairs have a much greater optical transition probability than the distant pairs.

Knowing the distribution of pairs and also the variation of capture cross section, and transition probability with pair separation, it should be possible to compute the change of shape of the continuously excited spectra with excitation intensity.

V. SUMMARY

This paper has been mostly concerned with a theoretical and experimental account of the kinetics of donor-acceptor pair recombination in gallium phosphide. Previous work has shown unambiguously that sharp lines seen in the low-temperature photoluminescent spectrum of GaP arose from pair recombination at nontypical close pairs, and that typical nonisolated pairs were responsible for the broad-"edge" emission of GaP. The broad emission is associated with distant pairs which have long radiative lifetimes. These account for the afterglow in a flash excited crystal which may last for many seconds, and which, at low temperatures has a decay rate independent of temperature. The over-all rate of light emission from the pair system can be calculated if the recombination rate is known as a function of the separation of the members of a particular pair, and if the distribution of these separations is known. In this paper, it has been assumed that the rate is an exponential function of the separation, with two parameters being required to define the rate, namely $W_{\max}$ and R_d. The distribution of pair separations is taken to be that corresponding to a random distribution of donors and acceptors, which will be the case in our crystals since the donors and acceptors cannot diffuse at low temperatures where pairing effects would be important. The simplest situation to consider is to suppose that all the donors and acceptors are neutralized with holes and electrons created by a pulse of excitation. With the assumptions just described the kinetics of the recombination of the immobile trapped carriers may be exactly calculated for the case in which either the donors or acceptors are in excess. An approximate solution is also given for the more difficult problem in which the donor and acceptor concentrations are equal. The decay of the total light from the system is nonexponential and greatly dependent on the concentration of the impurities. Over certain ranges of time and concentration the light intensity falls off inversely with time. Comparisons of the theoretical results have been made with the experimentally observed decay of suitably doped GaP crystals excited by 350-keV pulses of electrons from a Van de Graaff accelerator. Good agreement between theory and experiment has been found for certain crystals over many factors of 10 in light intensity and time. Reasonable values of $W_{\max}$ and R_d were deduced. For more heavily doped crystals, as expected, the emission decayed more rapidly than for lightly doped crystals, however the spectral output showed that complications arose in the chemical doping of the crystals and so complete quantitative agreement with theory was not obtained. The decay of the total light from systems in which all the donors and acceptors were *not* initially neutralized showed that the capture cross section of pairs with a small separation was less than that of pairs with a large separation. The cross section was found to vary approximately as the square of the separation.

Calculations and observations were made of the spectra at different times during the decay and again reasonable agreement was observed between experiment and theory. The spectra changed during the decay because close pairs decay at early times and distant pairs at long times, and different pairs radiate at different energies. Not all the spectral broadening can be ascribed to this effect; there is a residual broadening which is attributed to phonon effects and Stark broadening of the pair emission, and this is included in the theory in an empirical fashion. Similar effects are seen in the continuously excited spectra, which vary with the intensity of the excitation. Such variations are common in emission from many semiconductors and receive a natural explanation in terms of pair recombination. The "edge" emission from CdS falls into this class. The effect of a magnetic field at very low temperatures on the kinetics of the decay has been calculated and observed.

Although the presence of the sharp pair lines in GaP makes the identification of the broad emission as pair radiation easy, it is likely that in many materials there is broad pair emission even though, for whatever reasons, pair lines are not seen. The results described here should make possible the identification of pair effects in such cases. In particular, nonexponential decays do not necessarily imply a wide distribution of trap depths and thermal detrapping of carriers, as has often been assumed. An alternative explanation can be provided quite naturally by a random distribution of donors and acceptors throughout the crystal.

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