lem. The absorption in the presence of the magnetic field is in general higher than for $H=0$ and it is a function of H. (ii) For τ as given by ionized impurity scattering, the integrals of the transport coefficients are too complicated to be evaluated analytically. The absorption coefficient in the presence of the magnetic field, with respect to its value without magnetic field, is lower at low frequencies and higher at high frequencies.

In both cases the absorption coefficient in the presence of the magnetic field becomes smaller than for $H=0$ before reaching the high-frequency limit, but these frequencies are beyond those of interest in ultrasonics.

* Partially supported by Advanced Research Projects Agency of the Department of Defense.

[1] K. W. Nill and A. L. McWhorter, J. Phys. Soc. Japan Suppl. **21**, 755 (1966).

[2] C. Hamaguchi, J. B. Ross, and R. Bray, Bull. Am. Phys. Soc. **14**, 353 (1969).

[3] V. Dolat and R. Bray, Phys. Rev. Letters **24**, 262 (1970).

[4] H. N. Spector, Solid State Phys. **19**, 291 (1967).

[5] C. Jacoboni and E. W. Prohofsky, J. Appl. Phys. **40**, 454 (1969).

[6] C. Jacoboni and E. W. Prohofsky, Phys. Letters **A28**, 765 (1969).

[7] P. N. Argyres and E. N. Adams, Phys. Rev. **104**, 900 (1956).

[8] L. M. Roth and P. N. Argyres, Semicond. Semimet. **1**, 159 (1966).

[9] M. H. Cohen, M. J. Harrison, and W. A. Harrison, Phys. Rev. **117**, 937 (1960).

[10] T. Holstein, Phys. Rev. **113**, 479 (1959).

[11] C. Jacoboni and E. W. Prohofsky, Phys. Rev. B **1**, 697 (1970).

[12] σ_0 is the dc conductivity of the sample in absence of the magnetic field. Its presence here is simply due to σ_0 and ω_r put in the expression inside the brackets in Eq. (3) to make it nondimensional.

[13] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington, D.C., 1964).

[14] In order to give a full picture of the present classical theory, also in the high-frequency limit, the curves are plotted up to frequencies higher than those existing in solids.

PHYSICAL REVIEW B VOLUME 2, NUMBER 12 15 DECEMBER 1970

Field-Dependent Photoinjection Efficiency of Carriers in Amorphous Se Films

H. SEKI

IBM Research Laboratory, San Jose, California 95114

(Received 10 July 1970)

A concept of a field-dependent photoinjection process has been developed and applied to the low-energy light data from photodischarge measurements reported by Pai and Ing, and by Tabak and Warter. The model involves a field-dependent photogeneration of free carriers based on a Poole-Frenkel-type effect. Comparison with data tends to support the idea that the intermediate states are excitons. It is shown that the derived expression for the photoinjection efficiency fits the available experimental data on holes rather well for the entire range of field at room temperature. Indications are that the expression is valid down to about 250°K. The low-field data is shown to be highly dependent upon the mobility and the recombination velocity. Based on the reported experimental data, the recombination velocity and the effective band gap are found to be 200 cm/sec and 2.65 eV, respectively.

INTRODUCTION

In recent papers Pai and Ing,[1] and Tabak and Warter[2] have reported some measurements indicating a field-dependent photogeneration of free carriers in the photodecay process of amorphous Se. In both cases they attempted to explain their results in terms of the Poole-Frenkel[3] effect, but could not account for their data quantitatively over the entire range of field. In this paper it is shown that by a modified interpretation which introduces the concept of a photoinjection efficiency, their results for low light energies can indeed be explained in terms of the Poole-Frenkel effect.

In the second section, the concept of photoinjection efficiency is developed, and in the third section the Poole-Frenkel effect is introduced into the generation efficiency for low-energy light. Comparison with the reported experimental data is presented in the fourth section.

FREE-CARRIER GENERATION RATE VERSUS INJECTION RATE

The essential point of this paper is to make a distinction between the free-carrier photogeneration rate and the free-carrier photoinjection rate. In view of this distinction, the data reported by Pai and Ing,[1] and Tabak and Warter[2] directly represents the latter rather than the former. It was pointed out by Many[4] that even if the free-carrier generation efficiency is unity, the injection current is dependent on the field, recombination velocity, and the mobility. Here the concept of a field-dependent generation rate has been added. It should be mentioned that Pai and Ing[1] attributed the low-field behavior of their data to

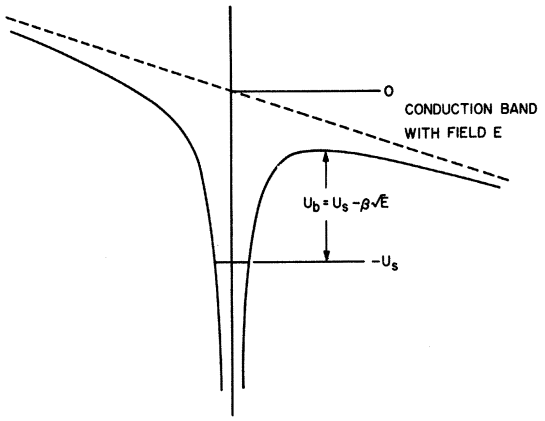

FIG. 1. Superposition of an applied field on a Coulomb potential for the Poole-Frenkel effect.

recombination although they did not include it quantitatively in their data analysis.

Neglecting the diffusion term and effects of trapping, the equation for the conduction current density is

$$j_c(x,t) = e\mu n(x,t) E(x,t), \tag{1}$$

where n is the carrier density, E is the field, e is the carrier charge, and μ is the mobility. For simplicity, it will be assumed that all the light is absorbed at the surface $x=0$. Since both holes and electrons are present at this surface during photoexcitation, a recombination process which is proportional to the free-carrier concentration is also assumed. The constant of proportionality is the effective recombination velocity v, which represents both surface and bulk recombination processes. Outside this region, since only one type of carrier is present, the recombination process can be ignored. If a field-dependent generation rate is assumed to be linearly dependent on the absorbed light, the boundary condition for the illuminated surface can be expressed as

$$j_c(0,t) = e\{fg(E) - vn(0,t)\}, \tag{2}$$

where f is the absorbed light in number of photons/cm^2 sec, and $g(E)$ is the free-carrier generation efficiency. Substitution of Eq. (2) into Eq. (1) gives

$$j_c(0,t) = ef\frac{E}{v/\mu + E}\, g(E), \tag{3}$$

where $E = E(0,t)$. The injection efficiency $y(E)$ is then defined as

$$y(E) \equiv \frac{j_c(0,t)}{ef} = \frac{E}{v/\mu + E}\, g(E). \tag{4}$$

POOLE-FRENKEL EFFECT AND GENERATION EFFICIENCY

In considering what form the generation efficiency might take we may expect intuitively that it must have a finite value less than 1 for zero field and at most approach unity for high field. We may further expect that at low fields, since we would expect the injection efficiency to be linear with respect to the field, the generation efficiency is more or less independent of the field. The expression derived by Tabak and Warter[2] from the Poole-Frenkel effect[3] satisfies this condition.

The Poole-Frenkel effect, also called the internal Schottky effect,[5] was initially derived by a simple one-dimensional analysis of the effect of an external field on the Coulomb potential of a fixed point charge. As shown in Fig. 1, if a charge carrier is bound at an energy level $-u_s$, the lowest potential barrier it must overcome to be ionized is decreased under an applied field E and is given by

$$u_b = u_s - \beta\sqrt{E},$$

where $\beta = (e/\pi\epsilon_0\epsilon)^{1/2}$, $\epsilon_0\epsilon$ being the dielectric constant and the energy is in eV. Frenkel postulated[3] that "if, in the absence of the electric field, the number of free electrons due to the thermal ionization of the atoms is proportional to $\exp(-u_s/2kT)$, where u_s is the ionization energy, the electrical conductivity in the presence of the field will be proportional to $\exp[-(u_s-\Delta u)/2kT]$." We quote this statement since in many papers which discuss the Poole-Frenkel effect[5–11] the 2 in $2kT$ is often omitted, and considered as the distinction with the Schottky emission.[12,13] We interpret the factor of 2 to enter from Fermi statistical consideration in the limit of large donor density or low T as discussed with thermal ionization of donors.[14] If the Fermi level is affected by the presence of other states this can be altered. Simmons[10] proposed a particular model of levels which kept the 2. Thus the incorporation of a Poole-Frenkel-type phenomenon in a solid should be considered not by itself but in context of the rest of the solid.

Pai and Ing[1] proposed that an effect similar to the Poole-Frenkel effect may apply to the exciton created by light. They were able to explain the high-field data for Se at low-energy light by assuming that the current is proportional to $\exp(\beta'\sqrt{E}/kT - u_s/kT)$ and found β' to be roughly $\frac{1}{2}\beta$ and $u_s = u_G - u_{ph}$, where $u_G = 2.47$ eV and u_{ph} is the energy of the incident light. Tabak and Warter assumed a steady state for the exciton density and derived an expression which they called η. It is this expression which has the property

TABLE I. Parameters for initial computation.

$A = v/\mu = 1.25\times10^3$	λ (Å)	u_{ph} (eV)	$B = \theta \times\exp[(u_G - u_{ph})/2kT]$
$\beta = (e/\pi\epsilon_0\epsilon)^{1/2}$	6200	2.000	6.61×10^4
$= 3.0972\times10^{-4}$	6000	2.066	1.49×10^4
	5800	2.138	5.32×10^3
$T = 300°$K	5500	2.254	7.91×10^2

we might expect for the generation efficiency. We have used the expression

$$g(E)=\{1+\theta\exp[(u_G-u_{ph}-\beta\sqrt{E})/2kT]\}^{-1},$$

where $\beta=(e/\pi\epsilon_0\epsilon)^{1/2}$, u_{ph} is the light energy, u_G is some effective band gap, and θ is a dimensionless constant. In terms of the steady-state model of Tabak and Warter, this assumes that the ratio of the rate of non-ionizing decay to the rate of ionization of the excitons is given by $\theta\exp(-u_b/2kT)$, where $u_b=u_G-u_{ph}-\beta\sqrt{E}$. The factor of 2 in the exponent is justified from experimental data as will be shown later. Combined with Eq. (4) we get for the injection efficiency

$$y(E)=\frac{E}{v/\mu+E}\left\{1+\theta\exp\left(\frac{u_G-u_{ph}-\beta\sqrt{E}}{2kT}\right)\right\}^{-1}. \quad (5)$$

According to the data reported by Spear,[15] the mobility of holes in amorphous Se is given essentially by the relation

$$\mu=35.8(T/300)^{3/2}\exp(-0.14/kT). \quad (6)$$

COMPARISON WITH EXPERIMENTAL RESULTS

The results reported by Tabak and Warter[2] in Fig. 9 of their paper, where "quantum efficiency" is plotted against the applied field, can be directly compared with our results. We have interpreted their "quantum efficiency" as the injection efficiency. First we tried

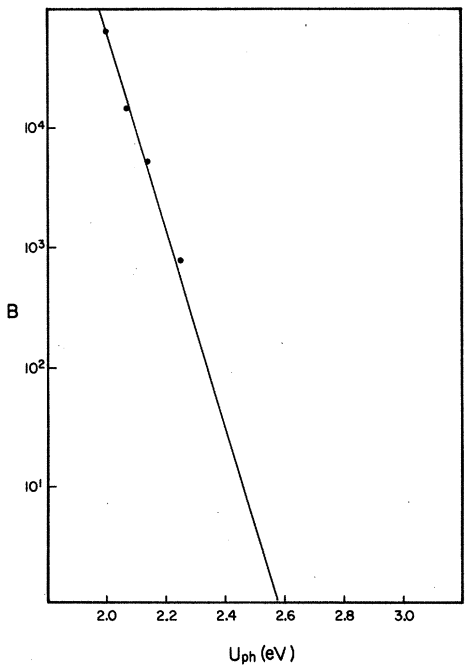

FIG. 2. $\theta\exp[(u_G-u_{ph})/2kT]$ obtained from initial curve fitting plotted against u_{ph}. The straight line has a slope of $-1/2kT$.

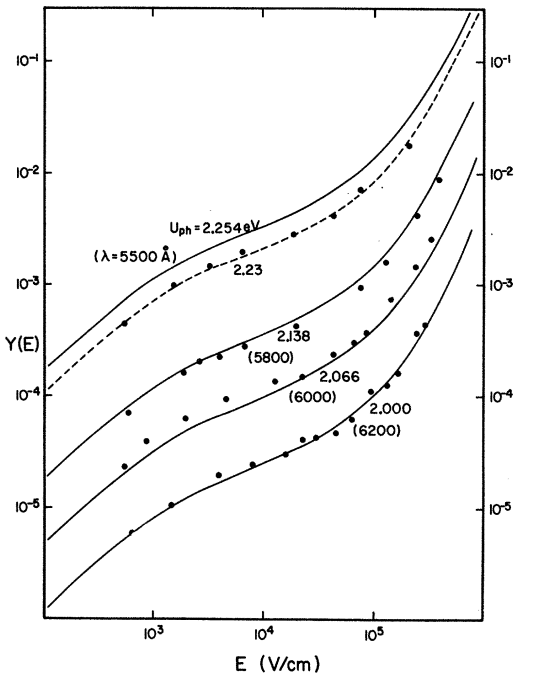

FIG. 3. Comparison of theory and experimental data for low-energy light. The curves are the injection efficiency calculated from Eq. (8) versus the field for $T=300°K$ for different wavelength and the data points were taken from Fig. 9 of Tabak and Warter's paper (Ref. 2).

to obtain a good fit using Eq. (5) in the form

$$y(E)=[E/(A+E)]\{1+B\exp(-\beta\sqrt{E}/2kT)\},$$

where $A=v/\mu$ and $B=\theta\exp[(u_G-u_{ph})/2kT]$. The values of the parameters obtained as a result of this fit are given in Table I. The value of $v/\mu=1.25\times10^3$ (V/cm) with Spear's[15] results for 300°K for the mobility gives the recombination velocity to be $v=200$ cm/sec. The value of v may vary from sample to sample, but is of the order of 10^2. Such variations will alter the low field values but will not affect the over-all shape of the curves. Note that this seems to be independent of the wavelength and suggests that no distinct recombination process occurs at the surface compared to the bulk. This value is also smaller than the values obtained by Many[4] for CdS. The fraction $E/(v/\mu+E)$ is similar in form to $E/(E_f+E)$ derived by Caywood and Mead[16] recently, but their E_f involves the absorption constant which would be wavelength dependent. Thus we must conclude that for these low light energies where the absorption coefficient is changing appreciably, the mechanism discussed by Caywood and Mead is not important.

Figure 2 is a plot of B against u_{ph} on a semilogarithmic graph. The slope of the line being $-1/2kT$ confirms that the denominator of the exponent is $2kT$ and gives

$$\theta\exp(u_G/2kT)=4.17\times10^{21}.$$

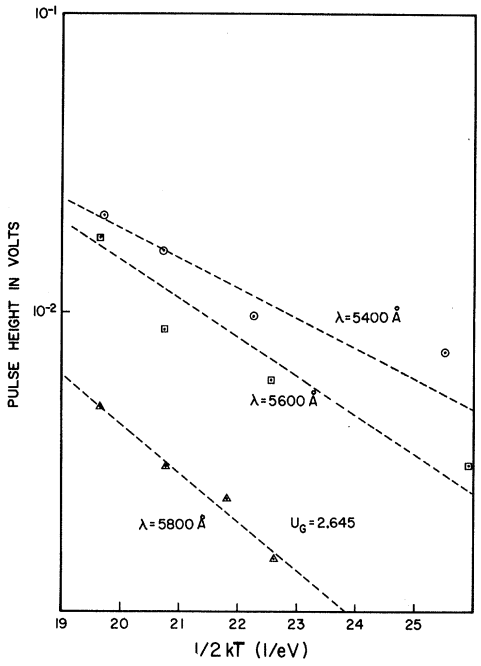

FIG. 4. Plots of pulse height taken from Figs. 2–4 of Pai and Ing's paper (Ref. 1) at $\sqrt{E}=4\times10^2$ $(V/\text{cm})^{1/2}$ against $1/2kT$.

Equation (5) can now be written as

$$y(E)=\frac{E}{1.25\times10^3+E}\times\left\{1+4.17\times10^{21}\exp\left(-\frac{u_{\text{ph}}+\beta\sqrt{E}}{2kT}\right)\right\}^{-1}. \quad (7)$$

In Fig. 3 we present a comparison of the data taken from Fig. 9 of Tabak and Warter's paper and Eq. (7) presented in solid curves. The computation was done at $T=300°\text{K}$ and the four curves were generated by varying just one variable u_{ph}. Except for the case $u_{\text{ph}}=2.254$ eV ($\equiv5500$ Å), the fit is rather good and supports our interpretation. The dashed curve which is a better fit to the data for $\lambda=5500$ Å was computed for $u_{\text{ph}}=2.23$ eV.

In order to establish θ and u_G we now refer to the temperature-dependent data of Pai and Ing.[1] Based on our interpretation, for $T\leq300°\text{K}$, $u_{\text{ph}}<2.4$ eV, and $E\leq2\times10^5$ V/cm, it can be concluded that

$$\theta\exp[(u_G-u_{\text{ph}}-\beta\sqrt{E})/2kT]\gg1.$$

Therefore for a given wavelength and electric field, the data should be proportional to $\exp(-u_G/2kT)$ if $E\gg v/\mu$. Figure 4 is a plot of the pulse height versus $1/2kT$ taken from Figs. 2–4 of Pai and Ing's paper at $\sqrt{E}=4\times10^2$ $(\text{V/cm})^{1/2}$, where $v/\mu\ll E$. The dashed lines represent slopes for $u_G=2.645$ eV which was obtained from the $\lambda=5800$-Å data. This value is larger than the value obtained by Pai and Ing. The corresponding value of θ becomes 0.2524. Hence the temperature-dependent injection efficiency for amorphous Se can now be expressed as

$$y(E)=\frac{E}{200/\mu+E}\times\left\{1+0.2524\exp\left(\frac{2.645-u_{\text{ph}}-\beta\sqrt{E}}{2kT}\right)\right\}^{-1}, \quad (8)$$

where μ is given by Eq. (6). For comparison, calculations based on this equation have been normalized to the room-temperature data at $\sqrt{E}=4\times10^2$ $(\text{V/cm})^{1/2}$ of Figs. 2–4 of Pai and Ing's paper and are presented with their data points in Figs. 5–7. As can be seen for room temperature the fit is quite good over the entire range of field. The fit for the lower temperature is fair and the general features are in agreement. Equation (8) assumes v, θ, and u_G to be temperature independent, but this may not necessarily be the case. If the transport of carriers is due to a hopping process and the longer duration of carriers in localized sites accounts for the lowering of the effective mobility at low temperatures, then since recombination will be less likely to take place if enough carriers of both polarity are in such sites, the recombination velocity may be effectively decreased at sufficiently low temperatures.

It can be seen that due to the effect of recombination the slope of the apparent linear region becomes greater for lower temperatures. Pai and Ing[1] assumed β to vary with temperature and determined this from the slopes and subsequently obtained u_G. This procedure accounts for the difference in their u_G and ours.

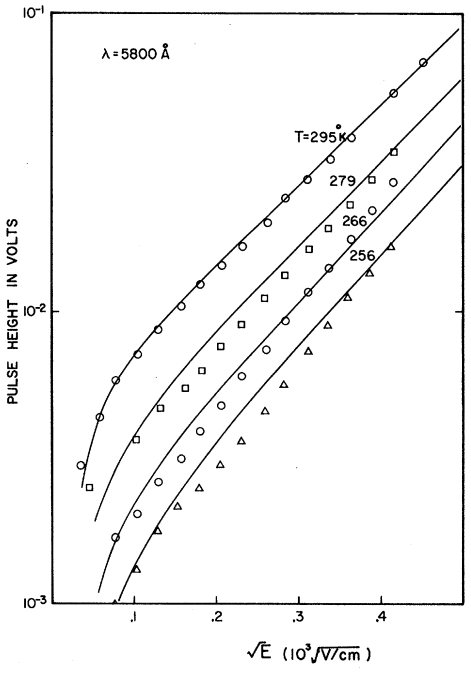

FIG. 5. Comparison of Pai and Ing's data for $\lambda=5800$ Å with Eq. (8) for various temperatures (°K).

Our final comparison is with the electron transport data given in Fig. 7 of Tabak and Warter's paper.[2] If the intermediate states in the photogeneration process are indeed excitions the expression for the generation efficiency should be the same for the electrons as well as for the holes. The recombination velocity should also be unchanged. In Fig. 8 we have reproduced the above data normalized to the unity gain value for $\lambda=5500$. The continuous curve was computed from Eq. (8) with $T=300°K$, $\mu=6\times10^{-3}$, and $u_{ph}=2.254$ eV. The fit is not as satisfying as the ones obtained for holes but we feel it is significant

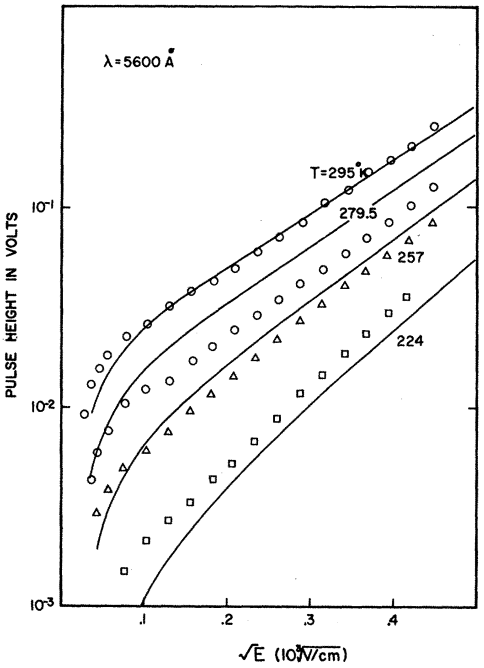

FIG. 6. Comparison of Pai and Ing's data for $\lambda=5600$ Å with Eq. (8).

that the calculated values are within about a factor of 2 of the data. A more detailed analysis taking into account the effects of trapping and detrapping may resolve the difference between theory and experiment but the difference in mobility between the hole and electron seems to account for the major difference in the magnitude of the respective injection efficiencies.

DISCUSSION

We have proposed that it may be useful to interpret the transport behavior of photoexcited carriers through a layer of photoconducting sample in terms of a photoinjection efficiency which in turn is proportional to a field-dependent photogeneration efficiency. This approach was applied to the data reported by Pai and Ing[1] and by Tabak and Warter[2] on amorphous

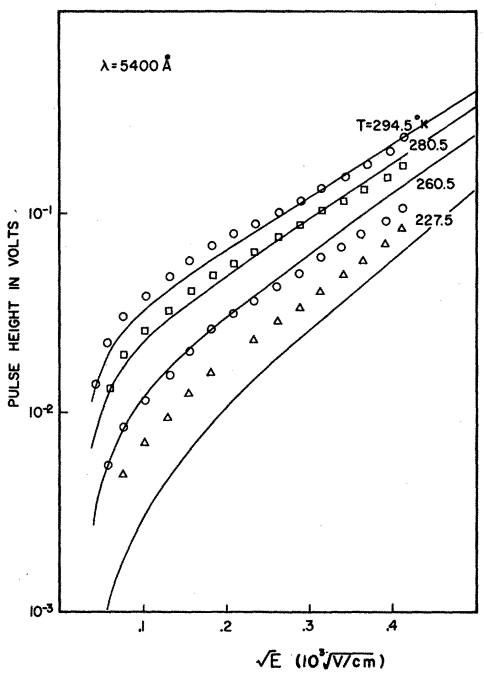

FIG. 7. Comparison of Pai and Ing's data for $\lambda=5400$ Å with Eq. (8).

Se films. Expressions were developed for the generation efficiency by assuming a Poole-Frenkel-type effect for the photogenerated excitons. The results indicate that there is a continuum of energy levels in these excitons. The model indicates how the mobility and recombination affect the injection efficiency. They are significant in the low-field range. And in the case of amorphous Se they play a very important role at low temperatures because of the rather drastic reduction of the mobility with temperature. The main difference

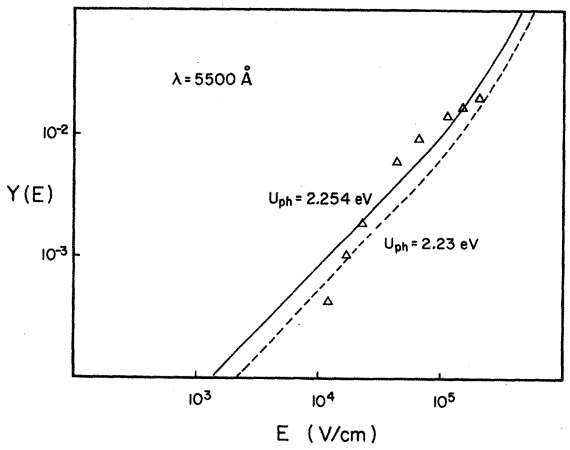

FIG. 8. Comparison of the electron data at $\lambda=5500$ Å taken from Fig. 7 of Tabak and Warter's paper (Ref. 2) with Eq. (8).

in the injection efficiency for electrons as compared to holes can be attributed to the difference in their mobilities. With this relatively simple model we have been able to quantitatively describe the essential features of the experimental results for low light energies.

Based on a simple interpretation of the results obtained so far the generation efficiency could be expected to be unity for energies greater than u_G. However, the data presented by Tabak and Warter[2] for $\lambda=4000$ and 4300 Å (Figs. 1 and 6 in their paper) show a rather striking kink at about $E=10^4$ V/cm from roughly linear to square-root dependence on the field which clearly indicates that the generation efficiency is not unity and is field dependent at these light energies. Actually in comparing the data of Pai and Ing[1] and Tabak and Warter[2] for high-energy light we are faced with a conflict. The data for $\lambda=4500$ Å in Fig. 8 of the former's paper shows the log of the pulse height to be proportional to $\sqrt{E}$ in the high-field region but the latter's data for $\lambda=4300$ Å indicate the peak photocurrent to be directly proportional to $\sqrt{E}$ in the same region.

At this point we can only speculate on the processes involved for light energies near the effective band gap u_G and greater. This will be an interesting area for further investigation. The exact relevance of the effective band gap u_G in our model and how it may be related to the activation energy involved in the expression for the mobility is an interesting question. We feel that the distinction between the photoinjection process and the photogeneration process will be useful in further investigation of the photodischarge process.

ACKNOWLEDGMENTS

I would like to express my thanks for the stimulating discussions and critical comments by my colleagues here, I. P. Batra, W. D. Gill, K. K. Kanazawa, R. M. Macfarlane, B. H. Schechtman, and B. D. Silverman. The support given by E. Kay has been most helpful in this work.

[1] D. M. Pai and S. W. Ing., Jr., Phys. Rev. **173,** 729 (1968).
[2] M. D. Tabak and P. J. Warter, Jr., Phys. Rev. **173,** 899 (1968).
[3] J. Frenkel, Phys. Rev. **54,** 647 (1938).
[4] A. Many, J. Phys. Chem. Solids **26,** 575 (1965).
[5] I. T. Johansen, J. Appl. Phys. **37,** 499 (1966).
[6] H. Hirose and Y. Wada, Jap. J. Appl. Phys. **4,** 639 (1965).
[7] C. A. Mead, Phys. Rev. **128,** 2088 (1962).
[8] T. E. Hartman, J. C. Blair, and R. Bauer, J. Appl. Phys. **37,** 2468 (1966).
[9] G. A. Dussel and R. H. Bube, J. Appl. Phys. **37,** 2797 (1966).
[10] J. G. Simmons, Phys. Rev. **155,** 657 (1967).
[11] A. K. Jonscher, Thin Solid Films **1,** 213 (1967).
[12] J. L. Hartke, J. Appl. Phys. **39,** 4871 (1968).
[13] Frederick Seitz, *The Modern Theory of Solids* (McGraw-Hill, New York, 1940), p. 161.
[14] Charles Kittel, *Introduction to Solid State Physics*, 2nd ed. (Wiley, New York, 1956), p. 358.
[15] W. E. Spear, Proc. Phys. Soc. (London) **76,** 826 (1960).
[16] J. M. Caywood and C. A. Mead, Appl. Phys. Letters **15,** 14 (1969).

PHYSICAL REVIEW B VOLUME 2, NUMBER 12 15 DECEMBER 1970

Phosphorus Clusters in ZnSe†

R. K. Watts and W. C. Holton
Texas Instruments Incorporated, Dallas, Texas 75222
(Received 13 July 1970)

The electron paramagnetic resonance of a center consisting of four phosphorus ions in ZnSe is reported. The paramagnetism is localized primarily on one phosphorus, and a smaller superhyperfine interaction with the other three is observed. The observed spin Hamiltonian parameters are $g_{||}=1.997$, $g_{\perp}=2.034$, $A_{||}=591\times10^{-4}$ cm^{-1}, $A_{\perp}=445\times10^{-4}$ cm^{-1}, $K_{||}=19.0\times10^{-4}$ cm^{-1}, $K_{\perp}<2.5\times10^{-4}$ cm^{-1}. The center has trigonal symmetry with a ⟨111⟩ axis, and the phosphorus ions are located at the points of a regular tetrahedron.

INTRODUCTION

The association of two or more atoms of the same kind in a compound semiconductor has been observed in several cases. Six fluorines can surround an iron in CdTe.[1] Four noble metals associate with an interstitial rare earth in CdTe[2] and ZnSe.[3] Rare-earth and 3*d* transition-metal fluoride molecules can be incorporated in ZnS.[4] Centers consisting of three associated lithiums have been observed in GaP,[5] and of two associated silicons in GaAs.[6] This paper reports observation by electron paramagnetic resonance of a cluster of four phosphorus ions in ZnSe.

EXPERIMENTAL PROCEDURES

ZnSe powder was compounded by allowing molten 6*N* pure zinc to react with a flowing stream of H_2Se gas. The powder produced was then sublimed in vacuum to a higher-density mass of more uniform stoichiometry. A small amount of phosphorus dopant was added, and single crystals were grown in a sealed ampoule by a gradient-freeze technique.[7] The volatility