Photon-Radiative Recombination of Electrons and Holes in Germanium

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The spectral distribution of the rate of photon generation for the photon-radiative recombination of electrons and holes in germanium is determined from known optical properties by application of the principle of detailed balance. Quantities characterizing the process are evaluated: The thermal equilibrium recombination rate at 300°K is 1.57×10^{13} cm^{-3} sec^{-1}, which corresponds to a recombination cross section of 2.9×10^{-21} cm^2 and a decay time for a small disturbance in carrier concentration in intrinsic material of 0.75 sec. The extension to the steady-state case of added current carriers is given, and estimates are included of the dependence of the quantities on temperature.

IT has been established that in the wavelength range from 1 to 2 microns photons absorbed in germanium produce electron-hole pairs with unit quantum efficiency.[1] The inverse process—the production of photons by electron-hole recombination—has also been observed.[2] In this paper, quantities characterizing this radiative recombination process are estimated for germanium by application of the principle of detailed balance to the thermal equilibrium rate of photon absorption estimated from the optical constants[3] at room temperature.

It should be remarked that recombination in germanium is in general so enhanced by imperfections, which have been referred to as "deathnium," that the lifetime of injected carriers is predominantly a structure-sensitive property and is much less than the lifetime for the radiative process alone.[4] Perhaps even in pure and perfect germanium crystals processes involving phonons and long-wavelength photons also occur and contribute materially to the reduction of lifetime. There is at present neither theoretical nor experimental information from which such contributions can be estimated.

From the principle of detailed balance, the rate of radiative recombination at thermal equilibrium for an elementary frequency interval $d\nu$ at frequency ν is equal to the corresponding rate of generation of electron-hole pairs by thermal radiation. This rate is $P(\nu)\rho(\nu)$ per unit volume and unit frequency interval, where $\rho(\nu)d\nu$ is the density in the crystal of photons in the range $d\nu$, and $P(\nu)$ is the probability per unit time that a photon of frequency ν be absorbed. The total rate $\mathfrak{R}$ per unit volume is obtained by integrating over ν as follows:

$$\mathfrak{R}=\int P(\nu)\rho(\nu)d\nu. \tag{1}$$

While the range of integration is nominally all values of ν, the principal contribution to the integral for germanium comes, as will be seen, from a comparatively narrow frequency range near the absorption edge.

With added current carriers, the total rate of radiative recombination $\mathfrak{R}_c$ per unit volume in the steady state is given by

$$\mathfrak{R}_c=(np/n_i^2)\mathfrak{R}, \tag{2}$$

since[5] it must be proportional to the product of electron concentration n and hole concentration p and be equal to $\mathfrak{R}$ when this product has its thermal equilibrium value, the square of the concentration n_i of electrons or holes in the intrinsic semiconductor.

From the expression for $\mathfrak{R}_c$, the decay time for a small disturbance in concentration if radiative recombination alone were operative may readily be calculated.[6] If δn and δp are small concentrations in excess of the steady-state values, (2) gives for the net recombination rate,

$$\delta\mathfrak{R}_c=(\delta n/n+\delta p/p)\mathfrak{R}_c, \tag{3}$$

whence the decay time for a relatively small[7] disturbance for which $\delta n=\delta p$ is

$$\tau=np/(n+p)\mathfrak{R}_c. \tag{4}$$

For sufficiently strongly extrinsic n- or p-type material initially at thermal equilibrium, with $n=n_0$ and $p=p_0$, τ from Eq. (4) equals, respectively, the microscopic lifetimes for minority holes or electrons.[6] With the thermal equilibrium minority carrier concentration negligible in each case, these lifetimes are

$$\begin{aligned}\tau_p&=p_0/\mathfrak{R}=2(p_0/n_i)\tau_i=2(n_i/n_0)\tau_i,\\ \tau_n&=n_0/\mathfrak{R}=2(n_0/n_i)\tau_i=2(n_i/p_0)\tau_i,\end{aligned} \tag{5}$$

where, from (4),

$$\tau_i=n_i/2\mathfrak{R} \tag{6}$$

[1] F. S. Goucher, Phys. Rev. **78**, 816 (1950); Goucher, Pearson, Sparks, Teal, and Shockley, Phys. Rev. **81**, 637 (1951).
[2] J. R. Haynes and H. B. Briggs, Phys. Rev. **86**, 647 (1952); R. Newman, Phys. Rev. **91**, 1313 (1953).
[3] H. B. Briggs, Phys. Rev. **77**, 287 (1950); J. Opt. Soc. Am. **42**, 686 (1952).
[4] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 69; Proc. Inst. Radio Engrs. **40**, 1289 (1952), pp. 1297 ff.
[5] Tacit in this reasoning is the assumption that the velocity distributions of electrons and holes are independent of the concentrations. Hence, (2) is strictly applicable only if the electron and hole gases are nondegenerate.
[6] W. van Roosbroeck, Phys. Rev. **91**, 282 (1953).
[7] It is assumed that δn and δp are small compared with $(n+p)$, in accordance with (35) of reference 6 written in terms of the steady-state concentrations n and p.

is the decay time in material of intrinsic conductivity. The recombination cross section σ is given by

$$\sigma = \mathcal{R}/n_0 p_0 v = \mathcal{R}/n_i^2 v, \tag{7}$$

where v is a relative velocity of thermal motion.

The thermal equilibrium distribution of photon density, $\rho(\nu)$, may be calculated in the usual way from the density distribution of normal modes in wave number or in K space, by applying the partition function for the harmonic oscillator to each mode. Since wave number is

$$K = n\nu/c, \tag{8}$$

where n is refractive index and c the speed of light, the density of modes in the frequency range $d\nu$ is given by

$$2\times 4\pi K^2 dK = (8\pi/c^3)[n^3(1+d\ln n/d\ln\nu)]\nu^2 d\nu, \tag{9}$$

which is that for free space multiplied by the quantity in square brackets. The photon density distribution is accordingly given by

$$\rho(\nu) = (8\pi\nu^2/c^3)[n^3 d\ln n\nu/d\ln\nu]/[\exp(h\nu/kT)-1]. \tag{10}$$

The probability of absorption of a photon per unit time $P(\nu)$ is calculated as follows: The absorption coefficient,

$$\alpha \equiv 4\pi n\kappa\nu/c, \quad \kappa \equiv \text{absorption index}, \tag{11}$$

is defined and measured in terms of the relative decrease in intensity for given thickness of material along the optical path. A wave packet moving along the path has a group velocity of

$$v_g = d\nu/d(1/\lambda) = (c/n)(d\ln\nu/d\ln n\nu). \tag{12}$$

Hence,[8]

$$P(\nu) = \alpha v_g = 4\pi\kappa\nu(d\ln\nu/d\ln n\nu). \tag{13}$$

From (10) and (13),

$$P(\nu)\rho(\nu) = (32\pi^2\kappa n^3/c^3)\nu^3/[\exp(h\nu/kT)-1]. \tag{14}$$

The total rate $\mathcal{R}$ of radiative recombination per unit volume at thermal equilibrium may, from (1) and (14), be written as

$$\mathcal{R} = 32\pi^2 c(kT/ch)^4 \int_0^\infty \frac{n^3\kappa u^3 du}{e^u-1}$$

$$= 1.785\times 10^{22}(T/300)^4 \int_0^\infty \frac{n^3\kappa u^3 du}{e^u-1} \text{ cm}^{-3}\text{ sec}^{-1}, \tag{15}$$

in which $u \equiv h\nu/kT$ is the variable of integration. The lower limit u_0 corresponds to the long-wavelength limit of the characteristic absorption band, about 2.2μ for germanium, at wavelengths exceeding which other mechanisms of absorption, such as absorption by conduction electrons, predominate.[9]

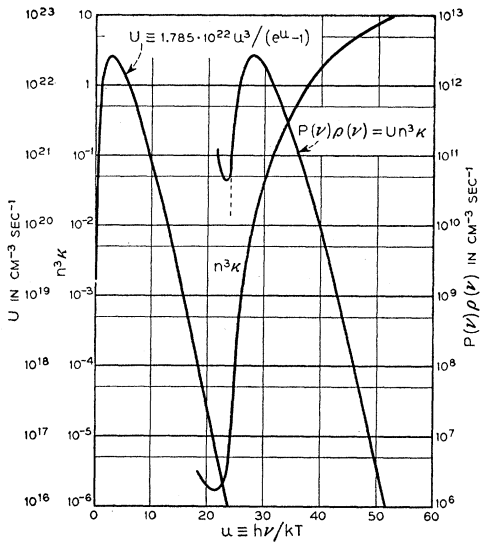

FIG. 1. The dependence for germanium of $n^3\kappa$ and the radiative recombination rate per unit frequency $P(\nu)\rho(\nu)$ on $u \equiv h\nu/kT$.

Values have been determined over the characteristic absorption band of germanium of the refractive index n and of the extinction coefficient $n\kappa$ for high-purity single crystals.[3] Using these values, the rate of recombination is found by numerical evaluation of the integral in (15) to be given by

$$\mathcal{R} = 1.57\times 10^{13} \text{ cm}^{-3}\text{ sec}^{-1} \tag{16}$$

at 300°K. While only the small fraction 7.7×10^{-8} of the photons at 300°K possess wavelengths below the long-wavelength limit for germanium,[10] it appears from the dependence on u of the integrand $P(\nu)\rho(\nu)$, shown in Fig. 1, that there is no appreciable contribution to $\mathcal{R}$ from the long-wavelength photons, the integrand possessing a sharp peak which occurs in wavelength just below the long-wavelength limit. In evaluating the integral, the contribution of carrier absorption, which causes the sharp increase in $n^3\kappa$ at the longer wavelengths, was obviated by using the dashed extrapolation shown in the figure.

In accordance with[11]

$$n_i^2 = 3.1\times 10^{32} T^3 \exp(-9100/T), \tag{17}$$

the corresponding lifetime and recombination cross

[8] This expression for $P(\nu)$ in terms of optical constants is readily derived also by considering the decay of a spatially unattenuated wave of given wavelength.

[9] J. Bardeen, Phys. Rev. **79**, 216 (1950); H. Y. Fan and M. Becker, in *Semi-Conducting Materials*, edited by H. K. Henisch (Butterworths Scientific Publications Ltd., London, 1951).

[10] U. S. National Bureau of Standards, *Miscellaneous Physical Tables: Planck's Radiation Function and Electronic Functions* (U. S. Government Printing Office, Washington, D. C., 1941), Applied Mathematics Series, Vol. MT-17.

[11] F. J. Morin (private communication); Phys. Rev. **93**, 62 (1954). At 300°K, n_i equals 2.4×10^{13} cm^{-3}, corresponding to an intrinsic resistivity of 47 ohm-cm for electron and hole mobilities of 3800 and 1820 cm^2 volt^{-1} sec^{-1}. See also reference 6, p. 288.

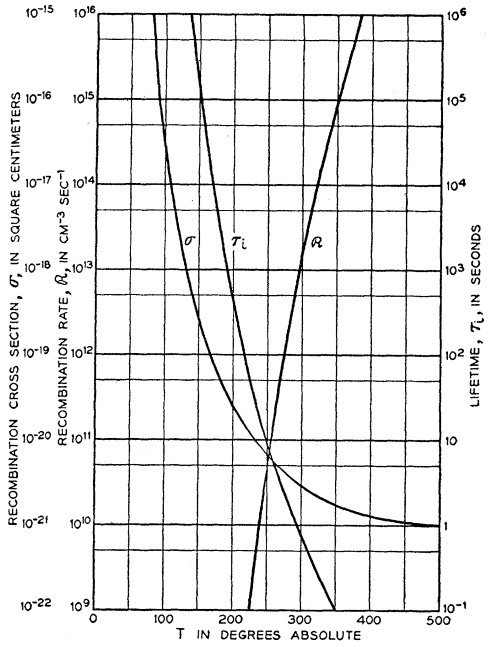

FIG. 2. The temperature dependence for germanium of the radiative recombination rate $\mathfrak{R}$, of the lifetime τ_i for intrinsic germanium, and of the recombination cross section σ.

section are, from (6) and (7),

$$\tau_i = 0.75 \text{ sec}, \quad \sigma = 2.9\times10^{-21} \text{ cm}^2, \tag{18}$$

at 300°K. For 10 ohm-cm n-type germanium at this temperature, τ_p is accordingly about 0.22 sec. Photon-radiative recombination thus has but slight influence in general on the observed lifetimes, which seldom exceed 10^{-2} sec.

Recombination radiation should be generated at the rate $(np/n_i^2)P(\nu)\rho(\nu)$ per unit volume per unit frequency interval, and such radiation from germanium was observed by Haynes and Briggs under conditions in which the emergent radiation should have essentially the same spectral distribution as that generated.[2,12] Their results are in good agreement with the $P(\nu)\rho(\nu)$ distribution of Fig. 1. Making correction for thickness of intervening material, Newman found radiation from germanium to be substantially in accord with theory.[2]

When the coupling between the electrons and the photons is large, application of the calculated $P(\nu)$ to a photon of frequency ν is not strictly correct. This approximation, however, introduces only relatively small error. For, it is evident from Fig. 1 that the principal contribution to $\mathfrak{R}$ comes from values of u less than 32; and for $u=32$, the photon intensity is attenuated in one wavelength in germanium by the factor[3]

$$\exp(-4\pi n\kappa/\lambda)(\lambda/n) = \exp(-4\pi/n)(n\kappa) \sim \exp(-2.4\times10^{-2}). \tag{19}$$

Thus, a photon is absorbed on the average in about 40 wavelengths, and the broadening of the photon levels by coupling with the electrons is only about 1.5 percent. It might also be remarked that the linearity resulting from quantum electrodynamics is such that absorption coefficients measured for cases in which there may be several photons in each mode are applicable to the present case, in which less than 10^{-7} of the modes are excited above the ground state.

Estimates of $\mathfrak{R}$, σ, and τ_i in their dependence on temperature are shown in Fig. 2. These estimates are based on the approximation that temperature changes the dependence of $n^3\kappa$ on ν only through the shift of long-wavelength limit associated with the temperature coefficient of the energy gap E_g. The data provide, with this assumption, the dependence at 300°K of $n^3\kappa$ on $h\nu/E_g$. With[13]

$$E_g = 0.785 - 1.0\times10^{-4}T \text{ ev}, \tag{20}$$

the curve of Fig. 1 of $n^3\kappa$ *versus* $u\equiv h\nu/kT$ is thus shifted along u axis in accordance with

$$u/u_{300} = 300/T + 0.040(300/T - 1). \tag{21}$$

The rapid increase of photon density with temperature produces the corresponding increase in $\mathfrak{R}$ and decrease in τ_i shown in Fig. 2; but it is the more rapid increase of n_i^2 that produces the decrease in σ, which appears to become substantially constant at the higher temperatures shown.

We are particularly indebted to Miss D. J. Oxman for evaluation of the integrals and to Mr. H. B. Briggs for his assistance with the optical data.

[12] Visible recombination radiation of a broad band width from silicon carbide, with photons of energies in general somewhat less than the value of the energy gap, has been observed: Lehovec, Accardo, and Jamgochian, Phys. Rev. **83**, 603 (1951); Phys. Rev. **86**, 615 (1952). See also K. Lehovec, Proc. Inst. Radio Engrs. **40**, 1407 (1952).

[13] See the text of reference 4, pp. 335–336.