

FIG. 1. Dependence of absorption constant on photon energy for silicon.

of indirect transitions<sup>1,2</sup> is the energy gap, varies with temperature as shown in Fig. 2. It behaves quadratically at low temperatures just as for germanium. We observe that our values for  $K$  agree substantially with those of Fan, Shepherd, and Spitzer<sup>3</sup> at room temperature.

From cyclotron resonance experiments<sup>4,5</sup> we know that the energy maximum of the valence band is at the origin and equal energy minima occur along the six  $[1,0,0]$  axes of momentum in the conduction band. According to the theory that the absorption tail

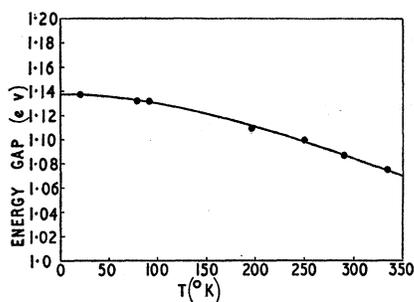


FIG. 2. Dependence of energy gap on temperature for silicon.

beyond the lattice edge is due to indirect transitions,  $k\theta$  is then the energy of the longitudinal acoustic wave with momentum equal to the momentum of the electrons at the minimum of the conduction band. From the known values of the elastic constants of silicon<sup>6</sup> and the theory of vibrations of the diamond lattice,<sup>7</sup> we estimate that the conduction band minima occur at a momentum of  $9.0 \times 10^7 \text{ cm}^{-1}$ , which is about 7/9 of the distance from the center to the edge of the Brillouin zone in the  $[1,0,0]$  direction.

We have attempted to correlate the intrinsic carrier concentration  $n_i$  of Morin and Maita<sup>8</sup> with our values of  $E_G$ . We find

$$n_i = 4.82 \times 10^{15} T^{3/2} (\bar{m}/m_0)^{3/2} N_c^3 \exp(-E_G/2kT),$$

where  $\bar{m} = 0.44m_0$  is calculated from the effective masses of holes and electrons<sup>4,5</sup> and  $N_c = 6$  is the number of energy minima in the conduction band. At  $T = 333^\circ\text{K}$  this gives  $n_i = 1.50 \times 10^{11} \text{ cm}^{-3}$ . Morin and Maita give data for  $n_i$  only above  $450^\circ\text{K}$  but if these data are extrapolated to  $333^\circ\text{K}$ , using their empirical formula, one gets  $n_i = 1.65 \times 10^{11} \text{ cm}^{-3}$ . The discrepancy is about 10 percent.

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<sup>8</sup> F. J. Morin and F. P. Maita, Phys. Rev. **96**, 28 (1954).

## New Radiation Resulting from Recombination of Holes and Electrons in Germanium

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**I**NTRINSIC radiation from germanium due to recombination of injected holes and electrons has been reported by Haynes and Briggs<sup>1</sup> and by Newman.<sup>2</sup> The results of these investigations show that the maximum of the energy radiated from the specimens used occurs at a wavelength of about  $1.8\mu$ . This result is in good agreement with that calculated by van Roosbroeck and Shockley<sup>3</sup> and by Newman<sup>2</sup> using the principle of detailed balancing and the optical absorption data of Briggs.<sup>4</sup> Recently, however, evidence has been found which shows that additional radiation is produced by a different recombination mechanism resulting in a second maximum at a wavelength of  $1.5\mu$ .

Evidence for this radiation was first found in the examination of radiation produced in germanium by a technique which is shown schematically in Fig. 1. The

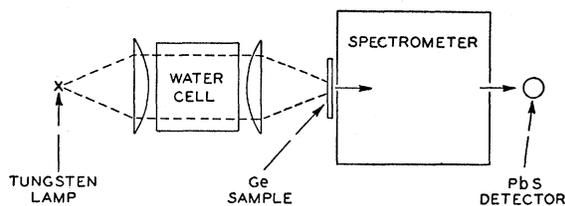


FIG. 1. Schematic arrangement used to measure recombination radiation as a function of wavelength.

light from a ribbon filament tungsten lamp was passed through a water absorption cell 10 cm long and focused on a thin slice of germanium ( $1.2 \times 10^{-2} \text{ cm}$  thick).

The radiation from the opposite side of the germanium was analyzed with a spectrometer and detected by a lead sulfide cell. Experiment shows that the water cell transmits less than  $10^{-10}$  of the incident radiation at wavelengths longer than  $1.4\mu$  and the germanium transmits less than  $10^{-10}$  of the radiation shorter than  $1.4\mu$ . It is therefore clear that no measurable light from the tungsten source will enter the spectrometer. Thus any detectable radiation must have its origin in recombination of electrons and holes produced by the light.

In this way, the intensity of the recombination radiation from the germanium sample was measured as a function of wavelength from  $1.3$  to  $2.1\mu$ . The results obtained were qualitatively in agreement with previous data obtained using  $p-n$  junctions biased in the forward direction. In this case, however, it is clear that the emergent radiation must be multiplied by a correction factor to take account of the rapidly varying absorption constant over the range of wavelengths considered. Since the diffusion lengths of the excess carriers were long compared to the sample thickness and the surface was treated to insure a low surface recombination velocity, it is reasonable to assume that both the minority carrier density and volume recombination take place uniformly throughout the sample thickness. Under these conditions the recombination radiation energy produced in the germanium,  $J_0$ , is given by

$$J_0 = J_{ad} / (1 - e^{-ad}), \text{ for } ad > 1,$$

where  $J$  is the measured emergent energy at a given wavelength,  $\alpha$  is the optical absorption constant, and  $d$  is the sample thickness.

When this correction was applied to the measured radiation using the absorption data of Briggs, the resultant curve shows a large second peak at about  $1.5\mu$ .

We were at first unable to understand this result since the principle of detailed balancing when applied to Briggs' absorption data gives no suggestion of such radiation. Recent data of Dash, Newman, and Taft,<sup>5</sup> as well as those of Fan, Shepherd, and Spitzer<sup>6</sup> show, however, that although the data of Briggs taken with single-crystal germanium are correct, his data taken with evaporated films ( $\lambda < 1.55\mu$ ) are not valid for single-crystal material.

Calculated values of the recombination radiation energy produced per unit volume as a function of wavelength, obtained by using this new absorption data and the analysis of van Roosbroeck and Shockley, are shown in Fig. 2. It is evident that in addition to the former maximum at  $1.75\mu$  a second peak at  $1.52\mu$  is obtained.<sup>7</sup>

It is difficult to show experimentally the existence of this second peak without resorting to the correction described, since the optical absorption for this radiation is high. Direct experimental evidence for its existence

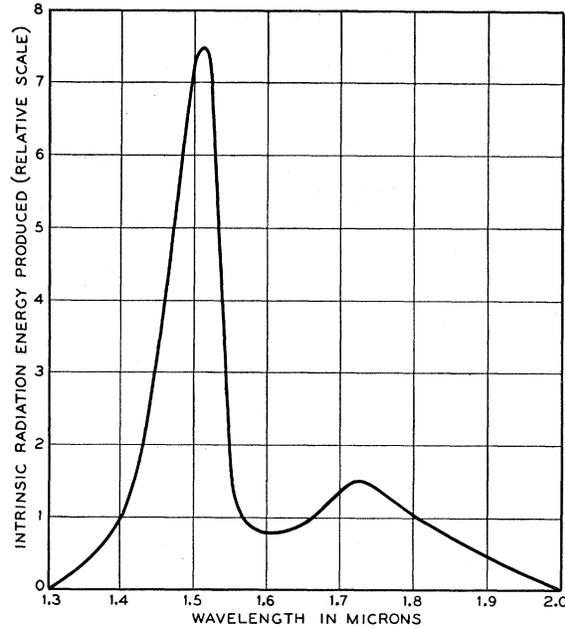


Fig. 2. Shape of radiant energy produced by the recombination of electrons and holes in germanium as a function of wavelength calculated using the optical absorption data of Dash, Newman, and Taft and the theory of van Roosbroeck and Shockley.

can only be obtained using specimens  $\sim 1 \times 10^{-3}$  cm thick or less.

Data obtained by using a germanium sample  $1.5 \times 10^{-3}$  cm thick are shown in Fig. 3, in which is plotted emergent energy as a function of wavelength. These data, corrected for absorption to give the photon energy produced per unit volume as a function of wavelength, are also shown in the figure by the dotted line. The

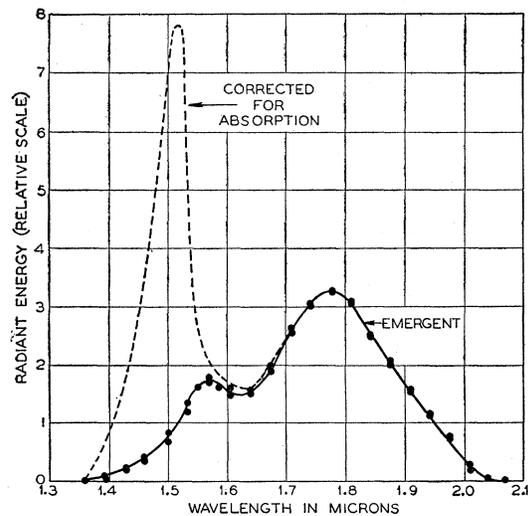


Fig. 3. Plot of experimental data obtained using a germanium sample  $1.3 \times 10^{-3}$  cm thick showing measured emergent radiation as a function of wavelength. The dotted curve was obtained from the solid line by correcting for absorption in the sample. (Data taken by using a  $p-n$  junction with forward bias.)

data leave no doubt that a double maximum exists in intrinsic recombination energy. The fit of the corrected curve to theory is probably as good as may be expected.<sup>8</sup>

This new radiation having a calculated maximum at  $1.52\mu$  (0.81 eV) is probably due to direct transitions at  $k=0$ , as has already been suggested for the corresponding absorption process,<sup>5,6</sup> while the radiation having a maximum at  $1.75\mu$  (0.70 eV) is due to indirect transitions involving phonon cooperation.<sup>9</sup> This suggests that the (000) minimum in germanium is only  $\sim 0.1$  eV above the (111) minimum.<sup>10</sup>

It is a pleasure to thank C. Herring for theoretical interpretation, J. A. Burton and J. A. Hornbeck for valuable discussions, and W. Flood and W. C. Westphal for the specimens and data.

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<sup>2</sup> Roger Newman, *Phys. Rev.* **91**, 1313 (1953).

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<sup>4</sup> H. B. Briggs, *J. Opt. Soc. Am.* **42**, 686 (1952).

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<sup>6</sup> Fan, Shepherd, and Spitzer, Conference on Photoconductivity (to be published).

<sup>7</sup> A further result of this additional radiation is to reduce the value of the lifetime of excess carriers in intrinsic material as calculated by van Roosbroeck and Shockley from 0.75 sec to 0.25 sec.

<sup>8</sup> Increased emergent radiation at longer wavelengths due to multiple internal reflections make the longer wavelength maximum too large compared to that at shorter wavelength by a factor of  $\sim 1.7$  or more, depending on whether the reflections are specular or partially diffuse.

<sup>9</sup> That the first absorption edge is indirect was pointed out by C. Herring [*Phys. Rev.* **93**, 943 (1954)] and is in accordance with the detailed theory of Bardeen, Blatt, and Hall [Atlantic City Photoconductivity Conference (to be published)].

<sup>10</sup> This agrees with theoretical estimates: see F. Herman, *Phys. Rev.* **95**, 847 (1954); R. H. Parmenter (unpublished).

## Overhauser Nuclear Polarization Effect

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THE degree of nuclear polarization which can be attained by the Overhauser<sup>1</sup> effect in metals or nonmetals depends on the nuclear spin relaxation mechanisms. We consider a system of nuclei and electrons in which the nuclei may relax by any or all of the following independent processes: (1) nuclear spin flip accompanied by an electron spin flip in the opposite sense, (2) nuclear spin flip accompanied by an electron spin flip in the same sense, and (3) nuclear spin flip without an accompanying electron spin flip. In the hyperfine contact interaction originally discussed in this connection by Overhauser, only the first type of relaxation occurs. In the dipolar part of the hyperfine interaction all three types of relaxation are present.

An application of the thermodynamic arguments of

Brovetto and Cini<sup>2</sup> leads to the following expression for the ratio of the populations of adjacent Zeeman levels:

$$\frac{M_m}{M_{m-1}} = \left[ \frac{1 - (1-s) \tanh|\gamma_e| \hbar H_0 / 2kT}{1 + (1-s) \tanh|\gamma_e| \hbar H_0 / 2kT} \right]^{(f^{(1)} - f^{(2)})} \times \exp[\gamma_n + (f^{(1)} - f^{(2)})|\gamma_e|] \frac{\hbar H_0}{kT}. \quad (1)$$

The quantities  $f^{(1)}$ ,  $f^{(2)}$ , and  $f^{(3)}$ , the sum of which is unity, denote, respectively, the fraction of nuclei relaxing by each of the three processes described in the foregoing, and  $s$  is the saturation parameter. When  $s=1$ , this expression reduces to that obtained by Kittel<sup>3</sup> on the basis of statistical arguments, and for other appropriate limiting values of  $s$  and the  $f$ 's it reduces properly to known results.<sup>††</sup>

The perturbation method of Overhauser may be applied to relaxation processes (2) and (3) as well as to process (1) and leads to the following expression for the ratio of populations:

$$M_m/M_{m-1} = 1 + \alpha + \frac{1}{2}\alpha^2 + \text{higher order terms}, \quad (2)$$

where

$$\alpha \equiv [\gamma_n + s(f^{(1)} - f^{(2)})|\gamma_e|] \hbar H_0 / kT.$$

To this order, Eq. (2) agrees with the corresponding expansion of Eq. (1), and with the expansion of  $\exp \alpha$ . Although these different expressions no longer agree for terms of order  $\alpha^3$ , for most purposes the use of the more convenient approximate form  $\exp \alpha$  is permissible. In addition the perturbation approach permits the calculation of the relaxation times, a possibility not afforded by the thermodynamic method. It should also be pointed out that although Eq. (1) appears reasonable in every respect, its derivation involves the application of classical thermodynamics to a system in a steady state rather than in a state of thermal equilibrium. We intend to discuss at a later time the justification of Eq. (1) on the basis of the thermodynamics of irreversible processes.

The only observations published thus far of the Overhauser effect [in metallic lithium<sup>4</sup> and in the  $\alpha, \alpha$ -diphenyl- $\beta$ -picrylhydrazyl (DPPH) free radical<sup>5</sup>] indicate that the enhancement of the nuclear population difference between adjacent Zeeman levels is about one order of magnitude smaller than the theoretically predicted value<sup>1</sup> of  $s|\gamma_e|/\gamma_n$ . In view of these results,<sup>6</sup> we were interested to see what effect the dipolar term in the hyperfine interaction had, and therefore calculated the value of  $f^{(2)}/f^{(1)}$  for metallic lithium using the wave functions of Kohn.<sup>7</sup> Although the Li wave function has a 73 percent admixture of  $p$ -state and only a 20 percent admixture of  $s$ -state, we found that  $f^{(2)}$  is less than 1 percent of  $f^{(1)}$ .

We would like to suggest the possibility in principle of a supplementary method of investigating exchange and correlation effects in metals. It is easily shown either from the free electron approximation or the Bloch