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## OPTICAL METHOD FOR DETERMINING CARRIER LIFETIMES IN SEMICONDUCTORS

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The mean lifetime of free carriers in a semiconductor is identical with the decay time of the photoelectric effect. The rise or the decay of the excess carrier density  $\Delta n$ , caused by illumination, is governed by the equation

$$\partial \Delta n / \partial t = Q - \Delta n / \tau. \quad (1)$$

$Q$  is the number of photons absorbed per unit volume and time, each photon giving rise to a hole-electron pair,  $t$  is the time, and  $\tau$  is the mean life of the carriers — electrons or holes. For the steady state, we obtain

$$\Delta n_s = Q_s \tau. \quad (2)$$

Besides increasing the electrical conductivity, the photoelectrically liberated carriers cause an increase in the infrared absorption of the semiconductor. This effect has been observed for germanium<sup>1,2</sup> and quite recently for silicon.<sup>3</sup> The transmittance due to the photogenerated free carriers is

$$T = \exp(-\Delta n \sigma l), \quad (3)$$

where  $\sigma$  is the absorption cross section (which is a function of the wavelength of the transmitted light) and  $l$  the length of the absorption path. The background transmittance is constant and may therefore be disregarded. Moreover, multiple reflections are ignored.

Suppose now that a constant illumination, leading to an excess carrier concentration  $\Delta n_s = Q_s \tau$ ,

is interrupted periodically. The relationship between the intensity of exciting illumination and time is thus represented by the curve I in Fig. 1. If there were no relaxation, this curve would also represent  $\Delta n$  as a function of time (with appropriate adjustment of the ordinate scale). If the mean life,  $\tau$ , of the liberated carriers is short or if the frequency of interruption,  $f$ , is low, then the real curve obtained from the solution of Eq. (1) with  $Q = 0$  and  $Q = Q_s$ , respectively, will deviate slightly from the rectangular shaped curve I. If on the contrary, the mean life is long or the frequency high, then the modulation of the illumination will cause a small ripple of the carrier density about the mean value  $\Delta n_s / 2$  (curve III in Fig. 1). In each case, the mean value of  $\Delta n$  is  $\Delta n_s / 2$ .

In the infrared wavelength region studied here, only thermal or pneumatic detectors are applicable for the measurement of the transmitted radiation. These have time constants of several hundredths of a second, whereas the mean lifetimes for the elementary semiconductors, germanium and silicon, amount at most to some milliseconds. For the high frequencies which are necessary for determining the lifetime in

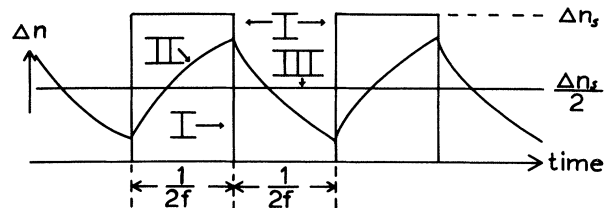


FIG. 1. Density of photoliberated carriers,  $\Delta n$ , as a function of time for periodically interrupted illumination. Curve I:  $f\tau \rightarrow 0$ ; Curve II: intermediate  $f\tau$ ; Curve III:  $f\tau \rightarrow \infty$ .

this case, the radiation detector will therefore measure a mean value  $\bar{T}$  over several periods rather than the instantaneous transmittance. This mean value will however, because of the nonlinear relationship between  $T$  and  $\Delta n$ , depend on the modulation frequency  $f$ . In one of the two extreme cases, when  $f\tau \rightarrow 0$ , where curve I in Fig. 1 can be applied, we obtain immediately

$$\bar{T}_0 = \frac{1}{2} \{1 + \exp(-\Delta n_S \sigma l)\} = \frac{1}{2} (1 + T_S), \quad (4)$$

whereas for the other extreme case,  $f\tau \rightarrow \infty$  (curve III):

$$\bar{T}_\infty = \exp(-\frac{1}{2} \Delta n_S \sigma l) = T_S^{1/2}. \quad (5)$$

For an intermediate value of  $f\tau$ , the solution of Eq. (1) with appropriate boundary conditions for each half period results in a curve like II of Fig. 1.

Obviously  $\bar{T}_0 > \bar{T}_\infty$ . The change in  $\bar{T}$  for continuously increasing  $f$  is shown in Fig. 2. Here  $\bar{T}$  on a linear scale is plotted against  $f\tau$  on a logarithmic scale.<sup>4</sup> The curve is computed for  $T_S = 0.64$ . The shape of the curve appears to be only slightly sensitive to an alteration in  $T_S$ .

Measurements according to the method outlined above were made on a sample of near-intrinsic germanium ( $\rho = 50$  ohm cm at room temperature) at the wave number  $900 \text{ cm}^{-1}$  using illumination from a tungsten strip lamp. The light from the lamp was chopped by a mechanical interrupter which could produce interruption frequencies up to about 5000 cps. The lower limit for  $f$  was set by the beam chopper frequency 13 cps of the spectrophotometer used. In practice, measurements were possible for  $f > 40$  cps. The fre-

quency was measured using an electromagnetic vibration indicator connected to an oscilloscope together with a calibrated audiofrequency generator.

For the determination of the mean life  $\tau$ , the experimentally obtained transmittances  $\bar{T}$  are plotted against the frequency  $f$  (on a logarithmic scale). The curve is then shifted horizontally until it fits the theoretical curve  $\bar{T}$  versus  $f\tau$ . A comparison between the two abscissa scales then immediately gives  $\tau$ . From Fig. 2, we see that, within the limits of error, the experimental plots do actually fit the theoretical curve, i.e., there is actually a constant mean life, which cannot be a priori postulated. The mean life obtained is  $\tau = 165 \mu\text{sec}$ , with an estimated error of  $\pm 20 \mu\text{sec}$ . This value was confirmed by several determinations performed with the infrared beam at different distances from the illuminated surface.

The infrared absorption of Ge at  $900 \text{ cm}^{-1}$  is due to the transition of free holes between the valence sub-bands. For the germanium sample investigated, the diffusion length for holes has previously been determined<sup>2</sup> from the infrared absorption and was found to be  $L = 0.14 \text{ cm}$ . The relationship

$$L = (D\tau)^{1/2} \quad (6)$$

then gives the diffusion constant  $D = 120 \text{ cm}^2/\text{sec}$ . This figure is not consistent with the well-established value for holes in germanium,  $D_p = 50 \text{ cm}^2/\text{sec}$  as obtained from mobility determinations,<sup>5</sup> and is only barely so with  $D_n = 100 \text{ cm}^2/\text{sec}$  for electrons in Ge. However, diffusion and recombination mechanisms may be far more complicated than assumed for the derivation of Eq. (6), e.g., because of the occurrence of trapping.<sup>6</sup> Among the possible applications of the method presented here, one should mention the possibility of determining both the lifetime and diffusion length for electrons and holes independently of each other, which may be useful for the experimental investigation of carrier properties in semiconductors.

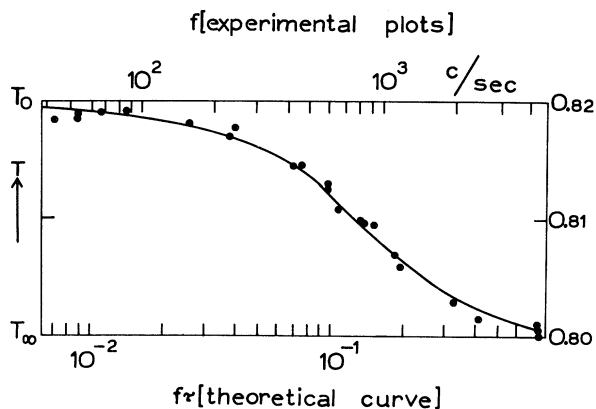


FIG. 2. Mean value of transmittance  $T$ , as a function of  $f\tau$  (calculated) and of  $f$  (measured for sample of intrinsic germanium).  $T_S = 0.64$  in both cases.

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<sup>2</sup>L. Huld and T. Staflin, Phys. Rev. Lett. **1**, 236 (1958).

<sup>3</sup>L. Huld and T. Staflin, Phys. Rev. Lett. **1**, 313 (1958).

<sup>4</sup>Details of the mathematical calculations will be

published elsewhere.

<sup>5</sup>M. B. Prince, Phys. Rev. 92, 681 (1953).

<sup>6</sup>A. K. Jonscher, Proc. Phys. Soc. (London) B70, 230 (1957).

### EXCHANGE SCATTERING IN SUPERCONDUCTORS

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In a recent letter,<sup>1</sup> Anderson and Legvold have suggested that the depression of the superconducting transition temperature of lanthanum as a function of rare earth impurity content<sup>2</sup> may be traced to the exchange interaction between the conduction electron spins and the  $f$ -shell spins of the rare earth ions. They postulate that the conduction electrons interact via the ionic spins to modify the effective "V" in the theory of Bardeen, Cooper, and Schrieffer. We wish to comment on this view in the light of theories by Herring and by ourselves, previously presented orally<sup>3,4</sup> and by now submitted for publication in detail, and in the light of the further experiments reported by Matthias, Suhl, and Corenzwit.<sup>5</sup>

Electron interaction via virtual states of the scatterers (in the present case the ionic spins) can occur only if these are nondegenerate in energy. In the case of gadolinium, the various spin orientations are very nearly degenerate, since its closed-shell configuration admits of very little crystal field splitting, and the effective electronic interaction is therefore likely to be very small. This point is further borne out by the experiments of Lynton, Serin, and Zucker<sup>6</sup> with nonmagnetic impurities, which also depress the transition temperature, yet interactions via virtual states of the scatterer are here essentially ruled out.

To summarize our own view, we begin with the magnetic impurities. We believe that the effect is indeed due to exchange scattering. However, the depression of  $T_c$  seems to us to result from the fact that the scattering lowers the energy of the normal state more than that of the superconducting state. Adopting the Bardeen-Cooper-Schrieffer view of the superconducting state, we find that those scatterings in which one or both of the initial and final momentum states are within the gap contribute more to the depression of the energy of the normal state than to the de-

pression of the energy of the superconducting state. The result is that as the impurity concentration is increased, the free energies of normal and superconducting states become equal, while the gap remains finite. A plot of transition temperature  $T_c$  versus impurity concentration  $\xi$  will not give a straight line but rather a convex curve with  $dT_c/d\xi=0$  at  $\xi=0$  and  $dT_c/d\xi=\infty$  at  $T_c=0$ . The value of the exchange integral required to account for the depression of  $T_c$  to absolute zero by the observed concentration of gadolinium in lanthanum is 0.15 volt, a reasonable value. As regards the shape of the curve, all cases, the newly measured ones (reference 5) as well as the (La, Gd) case seem to tend towards vertical tangency as  $T \rightarrow 0$ , in accord with the above predictions and at variance with a "shifted V" theory. A possible reason why at  $\xi=0$  the tangents to the  $T_c=\xi$  curves are not zero will become clear in connection with our next topic, scattering by nonmagnetic impurities. In that case, we find that the free energies of the normal and superconducting states are depressed much more nearly equally; for the same magnitude of the scattering potential, the difference is an order of magnitude less than in the exchange case. The difference then has the same form that one would have obtained, had one assumed the Bardeen-Cooper-Schrieffer expression for the free-energy difference in the impure sample, and attributed the change in this difference to a reduction in the effective interaction potential. This change is effectively a consequence of the modification of the electron wave functions by the impurities. Thus it could happen in the nonmagnetic case, that the free-energy difference goes to zero by virtue of the gap going to zero with increasing concentration. Whether this is the case, or whether the difference goes to zero before the gap does, is now a question of detailed evaluation. In the exchange case there is also such a shift in effective  $V$ , but there its effects can be important only along a short initial stretch of the  $T-\xi$  curve, where  $dT/d\xi$  tends to zero, while the shift in  $V$  produces a small but finite initial slope.

To summarize: If the Bardeen, Cooper, and Schrieffer theory of superconductivity is correct in its present form, the most important cause of the depression of  $T_c$  by exchange scattering is the disparity in the free-energy depressions of the normal and superconducting states. "Shifted V" effects, whether due to changes in wave function or due to electron interactions via