one energy. It is not necessary that

$$\frac{dg}{dE}=\sum_j \int_S \frac{\partial g}{\partial k_j}\frac{\partial k_j}{\partial E}\,ds,$$

with the integral performed over a surface of constant energy, be positive for some such surface. The necessary condition for negative resistance in the i direction only demands that $\partial g/\partial E$ along some line in the i direction be positive. In Ge and Si with warped heavy-hole bands, the necessary reversal may only correspond to a redistribution from the thermal equilibrium distribution along constant-energy surfaces.

Most of these conclusions were simultaneously and independently reached by Dr. C. Kittel. I am very grateful to him for making his results available. I would also like to thank Dr. F. Herman for several discussions.

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BIMOLECULAR ELECTROLUMINESCENT TRANSITIONS IN GaP

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In this Letter we describe direct observations of bimolecular band-to-band transitions at rectifying junctions in single crystals of gallium phosphide and indium phosphide.

The presence of bimolecular recombination kinetics is deduced from the nearly square dependence of the emitted radiation on the injection current. Additional evidence for band-to-band electroluminescence is supplied by an analysis of the spectral distributions of the absorption coefficient, the electroluminous emittance, and the photovoltaic response of gallium phosphide crystal rectifiers. These band-to-band radiative transitions differ in a number of ways from those occurring via localized levels.[1]

The above-mentioned square dependence has been discussed by van Roosbroeck and Shockley[2] and looked for without success in germanium by Newman[3] who found a linear dependence. So far only Aigrain and Benoit[4] observed a square dependence in germanium, when a very sensitive detection technique was used. Braunstein,[5] who investigated band-to-band radiative transitions of injected carriers in Ge-Si alloys, GaAs, GaSb, and InP, found a linear dependence in all cases, in agreement with Newman's observations.[3]

Our GaP samples were grown by I. Hegyi of these Laboratories from gallium solution by the method of Wolff, Keck, and Broder[6] using a 5-day programmed heat-cool cycle with a peak temperature of about 1200°C. The crystals were flat hexagonal platelets with major faces parallel to (111) planes and an area of a few square millimeters. They were a few tenths of a mm thick. The crystal structure, determined by J. White, was that of sphalerite with a lattice constant of 5.449 A. The impurity with the highest concentration was copper with approximately 5-50 parts per million. Care was taken to avoid using crystals that had inclusions of free gallium or free phosphorus.

Undoped GaP crystals appear to contain grown junctions beneath the surface, which resemble somewhat those found in single crystals of silicon carbide grown by commercial processes.[7] A highly n-type conducting layer is separated from the bulk by a rectifying junction and most likely also by a nearly intrinsic layer. Ohmic contacts to the crystal bulk can be made by alloying indium through the junction or by electrical burnout of the junction layer.

The opto-electronic characteristics of the rectifiers were displayed directly on an oscilloscope. The radiation was detected by RCA 1P21 and 7102 multiplier phototubes after having been spectrally analyzed by a Perkin Elmer monochromator. Transmission data were obtained using a model 14M Cary recording spectrophotometer.

Figure 1 is a photograph of five oscilloscope traces displaying the mutual and time dependence of the GaP rectifier parameters light (L), current (I) and voltage (V) for a 60-cps sinusoidal 8-volt rms excitation. Trace A is a plot of L vs I, which shows essentially a square depen-

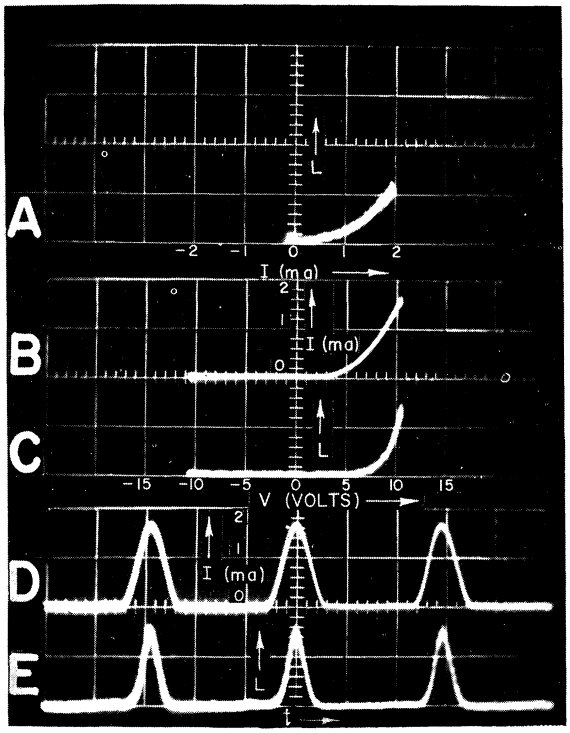

FIG. 1. Photographs of oscilloscope signals obtained from an electroluminescing GaP crystal rectifier. *A*—electroluminous emittance vs current; *B*—current vs voltage; *C*—electroluminous emittance vs voltage; *D*—current vs time; *E*—electroluminous emittance vs time.

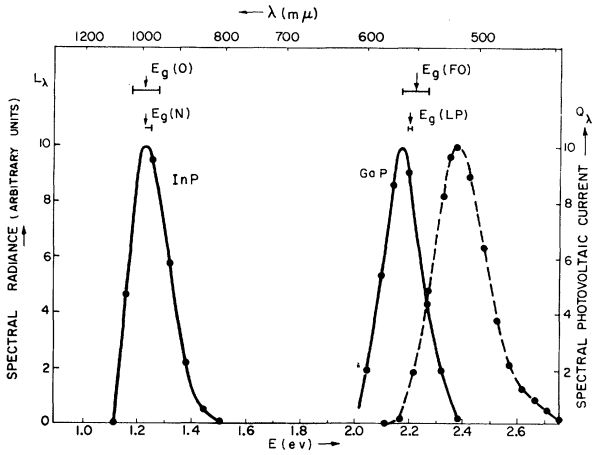

FIG. 2. Spectral opto-electronic responses of GaP and InP. Radiance indicated by ——. Short-circuit photovoltaic current indicated by ----. Letters in parenthesis indicate the following workers and references: O—Oswald (reference 13); N—Newman (reference 13); FO—Folberth and Oswald (reference 9); LP—Loebner and Poor (this Letter).

dence of light on current. Traces *B* and *C* show the *I-V* and *L-V* characteristics, respectively. It is seen that current and light appear only on the forward bias portion of the cycle. Traces *D* and *E* show the time dependence of *I* and *L*, respectively. The light at all times is perfectly in phase with both the current and the voltage.

Microscopic observations show the light to be emitted uniformly over an area of about 10^{-3} cm^2 from a depth of several microns below the surface. In the cases on hand, only the light clearing the electrode whisker participates in the data contribution.

Various results pertaining to the spectral characteristics of our samples are seen in Fig. 2. Our optical absorption measurements lead us to a room temperature estimate of an energy gap value for GaP of 2.20 to 2.21 ev. This estimate results from a fit of the Macfarlane-Roberts expression[8] to an α vs h plot for values of the absorption coefficient, α, between 10 and 150 cm^{-1} at several temperatures. Assuming the presence of a single phonon assisting in the optical transition, its energy is estimated to be 0.026 ev, which gives an equivalent temperature of about 300°K. Excess absorption at lower energies and higher temperatures is probably due to optical transitions at dislocations or some other crystal imperfections. As seen from Fig. 2, the energy gap value obtained by us is in good experimental agreement with that quoted in the literature.[9]

The dashed curve on Fig. 2 represents the spectral response of the short-circuit photovoltaic current in the same junction for which the electroluminous spectrum has also been obtained. The photoelectric current flows in the direction opposite to that producing electroluminescence, while the photovoltage has the same polarity as that producing electroluminescence, in agreement with the cases of SiC and CdTe.[10] The analysis of the photocurrent spectral response is identical to that of Wysocki, Loferski, and Rappaport.[11] For $h\nu$ just greater than E_g, $\ln(Q_{\lambda max} - Q_\lambda)$ is plotted against α. This gives a straight line, whose slope, 10^{-2} cm, is a measure of the distance that the photons pass through GaP. The relatively rapid falloff of Q_λ at high energies indicates a carrier diffusion length very much shorter than 10^{-2} cm.[11]

The spectral radiance of the very same GaP rectifier during electroluminescence is also seen on Fig. 2. The radiation peaks at photon energies

of 2.20 ± 0.02 ev with a half-width of a few kT. This value is a few hundredths of an electron volt lower than the peak obtained from the van Roosbroeck-Shockley theory[2] using the calculated α's (derived from the Macfarlane-Roberts analysis), but agrees well with the peak obtained using the above-discussed additional low-energy absorption. It is interesting to note that a comparison of the high-energy side of the spectral curve of electroluminous emittance to the van Roosbroeck-Shockley theory indicates a photon travel through GaP of about 10^{-2} cm. This is in rather good agreement with the value obtained from the photocurrent vs $h\nu$ analysis. Some of the additional low-$h\nu$ emission is most likely due to defect sites mentioned above. These and self-absorption cause the peak to shift somewhat to lower energies.

We conclude that most of the electroluminescent phenomena on hand are quite distinct from those originating from recombinations via defect states as reported previously.[1,12] In all the latter cases the photon distribution peaks at energies lower than the energy gap value obtained from free carrier recombination electroluminescence reported in this Letter, or from the analysis of other optical data. Also in all defect center recombination cases a linear dependence of the light on current has been found. The agreement between the above-discussed characteristics of electroluminescence, optical absorption, and photoelectric response leads us to identify the electroluminescent phenomenon as one primarily due to band-to-band bimolecular transitions.

We have also seen bimolecular recombination kinetics for radiative transitions of carriers injected across a rectifying junction in indium phosphide. Braunstein[5] reported the presence of recombination radiation in InP at an energy close to the band gap. We have obtained the spectral distribution of this radiation. It is shown in Fig. 2. The position of the peak at 1.25 ev is in good agreement with the band gap values reported in the literature.[13]

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ELECTRON SPIN RESONANCE EXPERIMENTS ON SHALLOW DONORS IN GERMANIUM

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Electron spin resonances on shallow donors in silicon have been studied by several authors.[1-3] In germanium there are various factors which make the observation of electron spin resonance signals more difficult and, so far, no resonances have been reported on shallow impurity states. The recent conflicting experimental results pertaining to the donor ground state in germanium[4,5] led us to reinvestigate the electron spin resonance behavior in this material. In the present Letter we wish to report on the observation of electron spin resonances from both bound and nonlocalized electrons in germanium. The results indicate that the ground state of the arsenic and phosphorus donors in germanium is a singlet.

The experiments were performed at temper-

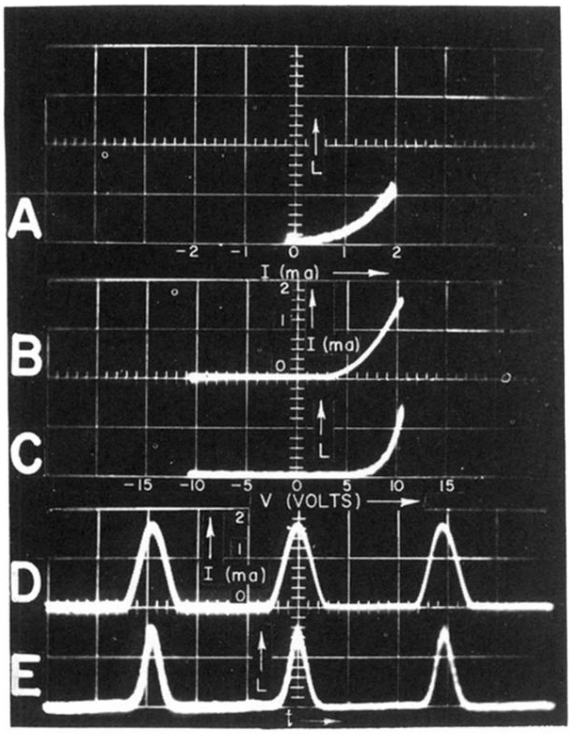

FIG. 1. Photographs of oscilloscope signals obtained from an electroluminescing GaP crystal rectifier. *A*—electroluminous emittance vs current; *B*—current vs voltage; *C*—electroluminous emittance vs voltage; *D*—current vs time; *E*—electroluminous emittance vs time.