Linde, Ann. Physik 15, 219 (1932); G. Borelius, Metallwirtschaft 12, 173 (1933); E. Grüneisen, Ann. Physik 16, 530 (1933); A. N. Gerritsen and J. O. Linde, Physica 18, 877 (1952); E. I. Salkovitz, A. I. Schindler, and E. W. Kammer, Phys. Rev. 107, 1549 (1957); D. K. C. MacDonald and W. B. Pearson, Acta Met. 3, 392 (1955); C. A. Domenicali and E. L. Christenson, J. Appl. Phys. 32, 2450 (1961); F. T. Hedgecock and W. B. Muir, Phys. Rev. 136, 561 (1964); J. S. Dugdale and Z. S. Basinski, Phys. Rev. 157, A552 (1967); A. Nakamura and N. Kinoshita (to be published).

[2]Grüneisen, Ref. 1; Gerritsen and Linde, Ref. 1; W. B. Pearson, Phil. Mag. 46, 911 (1955) (footnote, p. 915); Domenicali and Christenson, Ref. 1.

[3]J. M. Ziman, Electrons and Phonons (Clarendon Press, Oxford, England, 1960), Chap. VII.

[4]N. F. Mott and H. Jones, The Theory of the Properties of Metals and Alloys (Clarendon Press, Oxford, England, 1936).

[5]See, for example, Ref. 3, pp. 357-360.

[6]M. J. Rice, to be published. It is shown that the retention of only the first derivative in the expansion of τ_0 is valid in the limit of small concentrations.

[7]For metals, $(\partial \ln \tau_{ep}{}^0/\partial\epsilon)_{\epsilon=\epsilon_F} \sim \epsilon_F{}^{-1}$.

[8]I.e., high compared with $T_0(c)$ but small compared with $T_S = (\hbar\omega_S/k_B a)$ (since we have neglected terms of relative size T/T_S).

[9]D. K. C. MacDonald, W. B. Pearson and I. M. Templeton, Proc. Roy. Soc. (London), Ser. A 266, 161 (1962). The dilute Au:Fe thermoelectric data can be represented at low temperatures by the formula $S = A(k_B/e)T/(T+T_0')$ [A. M. Guenault, quoted by J. Kondo, Progr. Theoret. Phys. (Kyoto) 34, 372 (1965)]. We took $A = 0.2$, $T_0' = 1°K$ for both of the alloys quoted in the text. This gives $a \sim 1$ at $T \sim 10°K$, and $a \sim 12$ in the low-temperature limit.

[10]We have checked this assumption by explicitly differentiating the theoretical formula for $\tau_0(\epsilon)$ obtained within the s-d exchange model. [See, for example, Y. Nagaoka, Progr. Theoret. Phys. (Kyoto) 39, 533 (1968).] The $\partial \ln \tau_0/\partial\epsilon$ formula differs from that rigorously obtained by evaluating the appropriate Onsager coefficients [K. Maki, Progr. Theoret. Phys. (Kyoto) 41, 586 (1969)] only by a numerical constant of the order of unity. We thank D. R. Hamann for a discussion of this point.

[11]Domenicali and Christenson, Ref. 1.

[12]Gerritsen and Linde, Ref. 1.

[13]M. J. Rice and O. Bunce, to be published. Similar effects will occur in the el-ph contribution to the thermal resistivity. More generally, we note that a strongly energy-dependent electron-impurity cross section will modify any "ideal" resistivity that results from inelastic electron scattering at low temperatures. Thus we expect corrections, similar to those found here for the el-ph resistivity, to result for the resistivities arising from electron-electron and electron-magnon scattering.

FAR-INFRARED RECOMBINATION RADIATION FROM IMPACT-IONIZED SHALLOW DONORS IN GaAs †

I. Melngailis, G. E. Stillman, J. O. Dimmock, and C. M. Wolfe
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173
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Radiation corresponding to transitions from excited shallow donor states and from conduction-band states to the donor ground state has been observed in impact-ionized GaAs at temperatures near 4.2°K. Spectral measurements show a main peak at a wavelength of 282 μ (4.4 meV), corresponding to a $2p \rightarrow 1s$ transition, and a broader continuum extending to higher photon energies. A total radiated power of 10^{-7} W has been measured corresponding to an external quantum efficiency of about 10^{-6}.

The far-infrared photoconductivity spectra of shallow donor states in high-purity epitaxial GaAs have been studied recently at temperatures near 4.2°K, and the Zeeman splitting of the donor levels has been measured in magnetic fields up to 50 kG.[1-3] In this Letter we report the observation of recombination radiation involving such states, as well as measurements of the emission spectra and of output power. To our knowledge the only previous evidence of recombination radiation asssociated with shallow impurity states was observed for impact-ionized germanium[4] at 4.2°K; however, the detected power was quite low (3×10^{-12} W) and no spectral measurements were reported.

The high-purity epitaxially grown GaAs samples used in the present work were similar to those studied in the photoconductivity experiments.[3,5] Most of the measurements were made on a 0.4-mm-thick epitaxial layer grown on a semi-insulating substrate. For this sample a shallow-donor concentration of $N_D = 2.5\times10^{14}$ cm^{-3} and a total acceptor concentration of $N_A = 1.6\times10^{14}$ cm^{-3} were determined from an analysis of the temperature dependence of the Hall constant using the usual single-donor statistics.

Ohmic contacts were made by alloying Sn along the two longer edges of the 5×6 mm sample. The sample was mounted in a gold-plated stainless-steel light pipe which was immersed in liquid helium.

At 4.2°K the conduction electrons in the GaAs sample are frozen out on the shallow-impurity states which have a measured thermal ionization energy of about 5 meV. When a small critical voltage (1.8 V for the 5-mm-long sample used) is applied, the carriers are released by impact ionization.[6] Following breakdown, the voltage generally drops to a lower value (1.1 V) and the current then increases by about six orders of magnitude at a nearly constant voltage as the number of carriers in the sample increases. When nearly all of the donors are ionized, the sample conductance approaches a limiting value. From previous studies of impact ionization in germanium,[7] the initial breakdown is expected to occur in a filament which grows laterally as the current is increased.

Two methods were used to measure the radiation. In the first experiment the GaAs emitter was mounted in the same light pipe with an InSb detector which was positioned in a 30-kG solenoidal superconducting magnet. The emitter was outside the magnet. Since the InSb photoconductivity peak shifts to shorter wavelengths as the magnetic field is increased,[8] the InSb detector can be used as a crude far-infrared spectrometer. In a second experiment, spectral measurements with a resolution of about 0.15 meV were made using a Michelson interferometer and a GaAs photoconductive detector. The epitaxial GaAs detector was mounted in liquid helium in a separate Dewar. Its peak detectivity was two orders of magnitude greater than that of the InSb detector; however, it had a long-wavelength cutoff at about 300 μ. In both experiments the emitter was pulse biased at a repetition rate between 260 Hz and 1 kHz and a duty cycle between $\frac{1}{10}$ and $\frac{1}{2}$. The detector output was measured with a lock-in amplifier.

Data obtained with the magnetically tuned InSb detector showed a single broad peak near 5 meV (250 μ). The emission spectrum obtained using the interferometer and a GaAs detector is shown in Fig. 1. The general shape of the emission spectrum resembles the photoconductivity spectra obtained on similar GaAs samples.[3] The narrow peak at 4.4 meV (282 μ) coincides in photon energy with the main photoconductivity peak which was clearly identified with a transition from the $1s$ ground state to the $2p$ excited state of the donor. Emission from the higher excited impurity states is broadened and merges with that from the continuum. The identification of the main emission peak was confirmed by Zeeman splitting of the $2p \rightarrow 1s$ line which was observed when the emitter was placed in a 7.5-kG magnetic field. The spacing of the magnetic levels agreed with that observed for the $1s \rightarrow 2p$ line in the photoconductivity spectrum.[3]

Transitions from conduction-band states are expected at energies higher than the calculated donor-ionization energy[3] of 5.86 meV indicated by an arrow in Fig. 1. Assuming that very nearly all of the donors are ionized by the current pulse, the electron concentration in the conduction band is 0.9×10^{14} cm^{-3}. For the electron effective mass[3] of $0.0665m_0$, these carriers, when thermalized in the conduction band at 0°K, would occupy states up to an energy of 1.1×10^{-4} eV from the band edge. Allowing for thermal broadening at 4.2°K, where $kT = 3.6\times10^{-4}$ eV, and for the spectrometer resolution of about 1.5×10^{-4} eV, the thermal electron spectrum could not be expected to extend more than about 0.5 meV beyond the band edge. The high-energy tail of the spectrum, which extends about 3 meV to the right of the arrow in the figure, must therefore be attributed to hot electron recombination. The energy of some of the electrons is expected to extend beyond the 5.86-meV donor-ionization energy, which is the approximate minimum energy needed by a conduction-band elec-

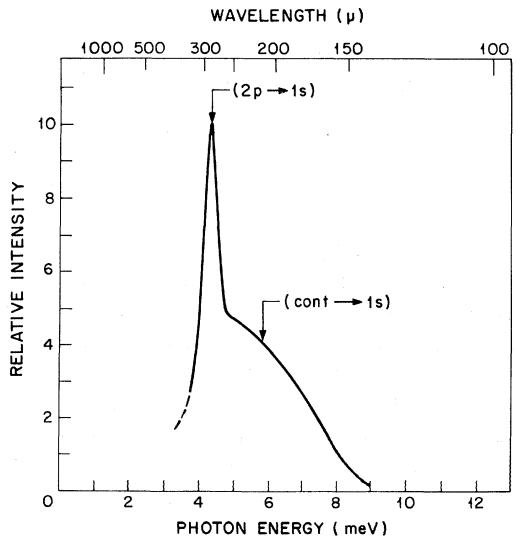

FIG. 1. Radiation spectrum of impact-ionized GaAs sample at 4.2°K biased with 260-μsec-long, 100-mA pulses at a 1-kHz repetition rate.

tron for impact ionization. To determine the role played by the electron distribution, the spectrum was measured at electric-field values of 2, 3, 6, and 8 V/cm. Since the increase in field produced no observable change in the spectrum, the hot electron distribution in the energy range up to 3 meV above the band edge must not change significantly with field in the range of field values used. It was also noted that the total emission intensity remained unchanged as the electric field was increased to 50 V/cm by applying short pulses to the sample. These observations are consistent with theoretical calculations and recent measurements of the mobility as a function of electric field.[9]

As indicated by a dotted-line extension at the low-energy end of the spectrum in Fig. 1, the GaAs detector cutoff near 4 meV would prevent observation of any lower-energy emission. However, since only one peak was observed with the InSb detector, which covers the low photon energy range, we can expect any such radiation to be considerably less intense than the $2p \rightarrow 1s$ peak.

Measurements of the radiated power were made by coupling the emitted radiation directly to the GaAs detector. The magnitude of the power was determined knowing the blackbody calibration and spectral response of the detector, the spectrum of the emitter, and losses in the light pipe. The variation of the total power with emitter conductance is shown in Fig. 2. At the higher currents, 20-μsec pulses were used in the emitter to avoid heating. A decrease in emitted power is evident with the 200-μsec pulses at currents beyond 50 mA. For currents greater than 100 mA, 60-Hz curve-tracer data indicated changes in the current-voltage characteristic associated with an increase of sample temperature. The nearly linear dependence of the radiated power on sample conductance seen in Fig. 2 is expected if a constant fraction of the ionized carriers recombine radiatively (constant quantum efficiency) and if mobility is independent of current. At currents below 30 mA mobility changes due to carrier heating are not expected, since up to this value the sample current increases at a very nearly constant voltage. In the model of filamentary breakdown,[7] the volume of the filaments increases as the current increases at constant voltage and the carrier density within the filaments remains constant. Thus mobility changes due to a variation in carrier density are not expected for filamentary breakdown, whereas such changes cannot be ruled out in the case of uniform

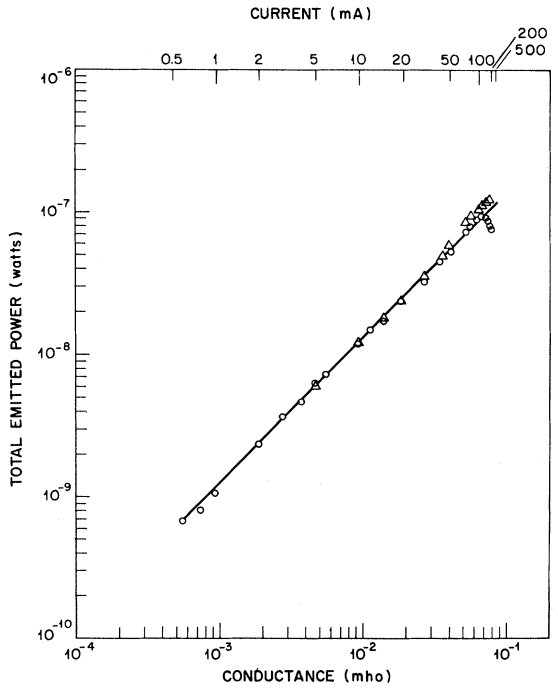

FIG. 2. Dependence of total radiated power on conductance of impact-ionized GaAs sample at 4.2°K. Current pulses 200 (open circles) and 20 μsec (open triangles) long were applied at a repetition rate of 1.5 kHz.

breakdown, where the carrier density increases with current.

A lower limit for the response speed of the emitter was obtained by observing the radiation pulses directly with an oscilloscope. A rise and fall time of 2 μsec was measured which was limited by the RC constant of the detector circuit.

The radiative lifetime for the transition of free carriers to the $1s$ state can be estimated from corresponding calculations for the hydrogen atom, as shown by Burstein, Picus, and Sclar.[10] By using the dielectric constant for GaAs of 12.5, the electron effective mass of $0.0665m_0$, the donor-ionization energy of 5.86 meV, the concentration of recombination centers $N_D = 2.5 \times 10^{14}$ cm^{-3}, and by assuming an electron temperature of 4.2°K, we obtain a radiative lifetime of 3.6×10^{-4} sec. The higher temperatures of a number of the electrons expected from the spectrum of Fig. 1 would yield an appreciably lower value for the average radiative recombination rate, and hence a longer lifetime. For the $2p \rightarrow 1s$ transition the radiative lifetime has a calculated value of 1.7×10^{-4} sec.

From measurements of the conductivity decay times following pulse excitation, we can estimate a lifetime for conduction-band electrons of about

7×10^{-9} sec which is much shorter than the calculated radiative lifetimes, indicating that the recombination is predominantly nonradiative. A recombination theory, in which conduction-band electrons cascade down to the ground state via excited states and lose their energy by emitting acoustic phonons, has been developed by Lax[11] and later improved by Hamann and McWhorter.[12] The later theory has given good agreement with measured recombination rates in germanium.[13] A recently reported observation of acoustic phonons generated in impact-ionized GaAs appears to confirm phonon generation as the main energy-loss mechanism.[14]

The quantum efficiency for direct radiative recombination of conduction-band electrons predicted from the ratio of the estimated carrier lifetime to the calculated radiative lifetime is about 2×10^{-5}. From the highest measured radiated power of 1.3×10^{-7} W, we estimate an external quantum efficiency of 1×10^{-6} by taking the ratio of the number of photons detected per second to the number of electrons recombining per second in the sample, which was obtained assuming that all of the donors are ionized ($n=0.9\times10^{14}$ cm^{-3}) and that the electron lifetime is 7×10^{-9} sec. The power efficiency, which is constant at currents up to nearly 30 mA, is 1.2×10^{-6}, very close to the estimated quantum efficiency. This number should in fact provide a lower limit for the actual quantum efficiency. The difference of an order of magnitude between the estimated external efficiency and the predicted internal efficiency of 2×10^{-5} cannot be accounted for by absorption losses in the 0.4-mm-thick sample, since the free-carrier absorption coefficient is estimated at about 0.6 cm^{-1} and the donor absorption in the fully ionized sample should be small. The estimate of the external efficiency may be low because it was obtained using the measured conductivity decay time after pulse excitation which should be appropriate for 4.2°K. In the emission experiments where a field of 2 V/cm or greater was present in the sample, the actual lifetime could be longer, due to hot-carrier effects. This would result in a higher value for the estimated external quantum efficiency. However, since the estimated carrier lifetime and the calculated radiative lifetime should both increase with increasing effective temperature, the predicted efficiency of 2×10^{-5} should be nearly independent of hot-electron effects.

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[1]D. R. Bosomworth, R. S. Crandall, and R. E. Enstrom, Phys. Letters 28A, 320 (1968).

[2]R. Kaplan, M. A. Kinch, and W. C. Scott, Solid State Commun. 7, 883 (1969).

[3]G. E. Stillman, C. M. Wolfe, and J. O. Dimmock, Solid State Commun. 7, 921 (1969).

[4]S. H. Koenig and R. D. Brown, III, Phys. Rev. Letters 4, 170 (1960).

[5]G. E. Stillman, C. M. Wolfe, I. Melngailis, C. D. Parker, P. E. Tannenwald, and J. O. Dimmock, Appl. Phys. Letters 13, 83 (1968).

[6]D. J. Oliver, Phys. Rev. 127, 1045 (1962); R. A. Reynolds, Solid State Electron. 11, 385 (1968).

[7]I. Melngailis and A. G. Milnes, J. Appl. Phys. 33, 995 (1962).

[8]M. A. C. S. Brown and M. F. Kimmitt, Brit. Commun. Electron. 10, 608 (1963); J. R. Apel, T. O. Poehler, and C. R. Westgate, Appl. Phys. Letters 14, 161 (1969).

[9]R. S. Crandall, Phys. Rev. (to be published).

[10]E. Burstein, G. Picus, and N. Sclar, in Proceedings of the Photoconductivity Conference, Atlantic City, N. J., 1954 (John Wiley & Sons, Inc., New York, 1956), p. 353.

[11]M. Lax, Phys. Rev. 119, 1502 (1960).

[12]D. R. Hamann and A. L. McWhorter, Phys. Rev. 134, A251 (1964).

[13]S. H. Koenig, R. D. Brown, and W. Schillinger, Phys. Rev. 128, 1668 (1962).

[14]R. S. Crandall, Solid State Commun. 7, 1109 (1969).