BAND-TO-BAND OPTICAL PUMPING IN SOLIDS AND POLARIZED PHOTOLUMINESCENCE

R. R. Parsons*
Ecole Polytechnique, 17 rue Descartes Paris Ve,† France
(Received 29 September 1969)

Band-to-band optical pumping of spin-polarized conduction electrons is demonstrated in p-type GaSb at 4.2°K by measurement of the degree of polarization of the photoluminescence. Significant electronic polarization [42 (±8)%] is achieved, and experiments with a weak transverse magnetic field yield the electronic lifetime $\tau = 6.0\ (\pm 0.7) \times 10^{-9}$ sec of the photocreated electrons.

We have observed optical pumping of spin-polarized conduction electrons in a solid by analyzing the degree of polarization of the photoluminescence. Our experiment is the analog of the well-known experiments on optical pumping of electrons between atomic states in a gas[1] or in localized states in a crystal.[2-4] The feasibility of band-to-band optical pumping of delocalized electrons in a solid has been recently demonstrated in silicon at 77°K by Lampel.[5] However, due to the indirect band gap and the unfavorable relaxation times in silicon, Lampel achieved a small electronic polarization 10^{-3}%. Furthermore, Lampel's use of the dynamic nuclear polarization to monitor the electronic polarization is restricted to those solids in which the nuclear spins are relaxed by the photocreated electrons. In our case we obtain a significant polarization of (42 ± 8)% by using a direct band-gap semiconductor at 4.2°K; our method of monitoring the optical pumping cycle is in principle very general, as we use the degree of polarization of the photoluminescence to directly measure the electronic polarization. The experiments were performed on p-type GaSb. The samples were grown without intentional doping: The hole concentration at room temperature was 1.5×10^{17} cm^{-3}. All experiments were performed in zero applied longitudinal magnetic field (the axis of quantization is in the direction of propagation of the pump light). The high efficiency of our optical pumping shows that the spin-relaxation time T_1 is long compared with the lifetime τ of the photocreated electrons. This lifetime $\tau = 6.0\ (\pm 0.7) \times 10^{-9}$ sec is measured by studying the optical-pumping efficiency as a function of transverse magnetic field.

Optical pumping in zero magnetic field.—The optical pumping cycle is considered as a succession of three independent processes. (i) Spin-polarized electrons are excited across the band gap with σ^+ or σ^- circularly polarized light. (ii) Spin-relaxation mechanisms tend to equalize the spin-up and spin-down populations. (iii) The electrons recombine with holes, emitting light.

The pump cycle is schematically shown in Fig. 1. To well define the excitation process (i) we use pump light of energy $0.810\ \text{eV} \lesssim h\nu \lesssim 0.817$ eV approximately equal to the (direct) band-gap energy $E_g \cong 0.812$ eV. As shown in Fig. 1, therefore, we selectively pump from the $\Gamma_{15v}{}^{3/2}$ valence-band maximum to the $\Gamma_{1c}{}^{1/2}$ conduction-band minimum.[6]

The polarization of the recombination light is used to observe the optical-pumping cycle. With the use of a special chopper which rotates a quarter-wave plate at 35 cps, we measure the degree of polarization $\rho \equiv |[L_F(\sigma^+) - L_F(\sigma^-)]/[L_F(\sigma^+) + L_F(\sigma^-)]|$, where $L_F(\sigma^\pm)$ is the intensity of the photoluminescence of polarization $\sigma^\pm$. With unpolarized or linearly polarized pump light we observe $\rho = 0$; for σ^+ or σ^- polarization, $\rho = 0.21$ (±0.04). For our GaSb samples the dominant photoluminescent peaks are due to recombination of

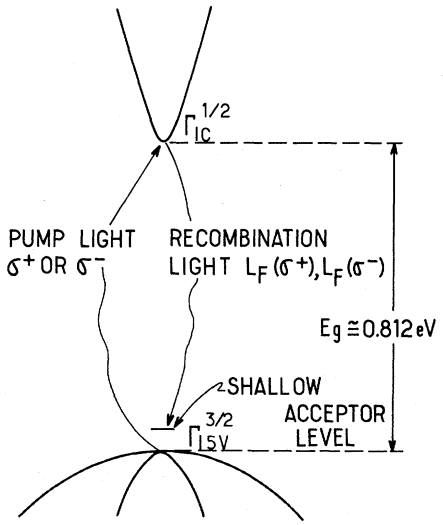

FIG. 1. The optical pumping cycle: excitation across the band gap with σ^+ or σ^- pump light, spin relaxation of the photocreated $\Gamma_{1c}{}^{1/2}$ electrons, and recombination emission involving shallow acceptor states. $L_F(\sigma^\pm)$ is the intensity of the photoluminescence of polarization $\sigma^\pm$.

photocreated electrons with bound holes.[7,8] Since the total number of holes ($\sim 10^{17}$ cm^{-3}) is very much greater than the number of photocreated holes ($\sim 10^{6}$ cm^{-3}), optical-pumping effects on the holes are negligible. By time-reversal symmetry, therefore, a nonzero ρ implies a nonzero electronic polarization $P \equiv |(n_+ - n_-)/(n_+ + n_-)|$, where n_+ and n_- are, respectively, the number of spin-up and spin-down conduction electrons. Thus, our observation of polarized photoluminescence ($\rho > 0$) with circularly polarized excitation light demonstrates band-to-band optical pumping of spin-polarized electrons. As required by Kramers conjugation, the differential spectrum $L_F(\sigma^+) - L_F(\sigma^-)$ reverses sign upon change of the polarization of the pump light from σ^+ to σ^-.

From our measurement of the absolute value of ρ we now determine the electronic polarization P and examine the ratio T_1/τ. The steady-state solution of the rate equations[5] gives

$$P = \frac{T_1}{T_1 + \tau} \left| \frac{g_+ - g_-}{g_+ + g_-} \right|, \qquad (1)$$

where g_+ and g_- are, respectively, the photoexcitation rates for spin-up and spin-down electrons with the absorption of σ^+ polarized pump light. The degree of polarization ρ of the photoluminescence is related to P by the equation

$$\rho = P |(r_+ - r_-)/(r_+ + r_-)|. \qquad (2)$$

Here, r_+ and r_- are, respectively, the recombination rates of spin-up and spin-down electrons with the emission of σ^+ polarized light. Since the recombination processes[7,8] of our photoluminescence involve conduction electrons with holes bound in shallow acceptor levels, in the effective mass approximation the recombination transitions are essentially band-to-band. Therefore, we make the approximation $|(r_+ - r_-)/(r_+ + r_-)| \cong |(g_+ - g_-)/(g_+ + g_-)|$. Calculating the relative $\Gamma_{15v}^{3/2} \rightarrow \Gamma_{1c}^{1/2}$ electric-dipole transition probabilities, one can show[9] that $|(g_+ - g_-)/(g_+ + g_-)| = 0.5$. Thus, from Eq. (2) and our measurement of $\rho = 0.21\ (\pm 0.04)$, we obtain $P = 42\ (\pm 8)\%$. This polarization is, within experimental error, the maximum polarization $P_{max} = |(g_+ - g_-)/(g_+ + g_-)| = 50\%$ which is only limited by the $\Gamma_{15v}^{3/2} \rightarrow \Gamma_{1c}^{1/2}$ matrix elements. By Eq. (1), $P = P_{max}$ implies that $T_1/\tau \gg 1$ (i.e., the spins do not have time to relax during the electronic lifetime). However, taking into account the experimental error in our determination of P we can only say that T_1 is at least twice greater than τ and probably much larger.

If the pump light is suddenly turned off, the magnetization associated with the electronic polarization P will decrease exponentially with the time constant T_{1e} given by $1/T_{1e} = 1/\tau + 1/T_1$. Since T_1 is long compared with τ, therefore, this magnetization time T_{1e} is approximately equal to τ. In the next section we use this result to deduce τ.

Optical pumping in transverse magnetic field.—As Fig. 2 shows, the degree of polarization of the photoluminescence is reduced by the application of a transverse magnetic field. This decrease in the optical-pumping efficiency is attributed to the Larmor precession of each photocreated electron during the magnetization time T_{1e}. The (Lorentzian) expression describing the decrease in electronic polarization P with a transverse field is[10] $1/[1 + (\omega_L T_{1e})^2]$; where ω_L is the electronic Larmor frequency. Figure 2 shows that the data are indeed described by a fit of a Lorentzian profile. Using the electronic g factor $|g| = 6.5$[11] and this curve fit, we obtain $T_{1e} = 6.0\ (\pm 0.7) \times 10^{-9}$ sec. Since our zero-field analysis has shown that $T_{1e} \cong \tau$, this measurement with a transverse field determines the lifetime $\tau = 6.0\ (\pm 0.7) \times 10^{-9}$ sec. This lifetime agrees with Habegger and Fan's[12] order of magnitude estimate $\sim 10^{-9}$ sec from transport studies. It is noted that τ and T_1 refer to electrons in the $\Gamma_{1c}^{1/2}$ conduction-band minimum in p-type GaSb at 4.2°K, and that τ is determined without measurement of absolute light intensities.

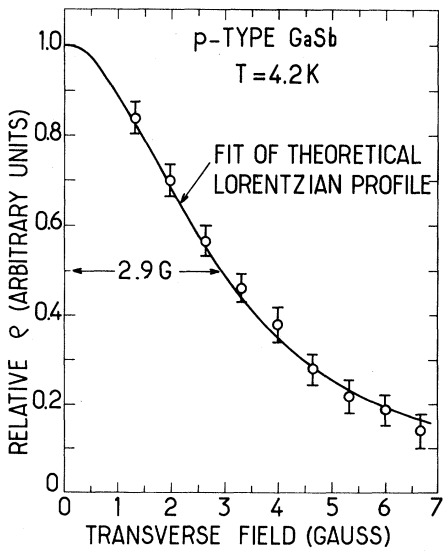

FIG. 2. The decrease of the optical-pumping efficiency with a transverse magnetic field. The degree of polarization ρ of the photoluminescence is proportional to the optically pumped electronic polarization.

We are presently extending our measurements to energies of the pump light greater than the band-gap energy. The author thanks Dr. G. Lampel for his constant interest and encouragement; also, it is a pleasure to thank Professor Solomon for very helpful discussions, and Dr. P. Lavallard and the other members of the Benoit à la Guillaume group for the loan of a sample and the use of their equipment.

---

*National Research Council of Canada post-doctoral Fellow.

†Equipe de Recherche du Centre National de la Recherche Scientifique.

[1]A. Kastler, J. Phys. Radium 11, 255 (1950).

[2]N. V. Karlov, J. Margerie, and M. D'Aubigne, J. Phys. Radium 24, 717 (1963).

[3]J. Brossel and J. Margerie, in Paramagnetic Resonance, edited by W. Low (Academic Press, Inc., New York, 1963), Vol. 2, p. 535.

[4]S. Geschwind, R. J. Collins, and A. L. Schawlow, Phys. Rev. Letters 3, 545 (1959); J. Brossel, S. Geschwind, and A. L. Schawlow, Phys. Rev. Letters 3, 548 (1959).

[5]G. Lampel, Phys. Rev. Letters 20, 491 (1968); and Proceedings of the International Conference on the Physics of Semiconductors, Moscow, U.S.S.R., 1968 (Nauka, Leningrad, U.S.S.R., 1968), p. 1139.

[6]For a description of the band structure of GaSb see: M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966); G. Dresselhaus, Phys. Rev. 100, 580 (1955); C. W. Higginbothman, F. H. Pollak, and M. Cardona, in Proceedings of the International Conference on the Physics of Semiconductors, Moscow, U.S.S.R., 1968 (Nauka, Leningrad, U.S.S.R., 1968), p. 57.

[7]E. J. Johnson, I. Filinski, and H. Y. Fan, in Proceedings of the International Conference on the Physics of Semiconductors, Exeter, England, 1962 (The Institute of Physics and The Physical Society, London, England, 1962), p. 375.

[8]P. Lavallard, thesis, presented at the Faculté des Sciences de l'Université de Paris, 1968 (to be published).

[9]G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the Thirty-Two Point Groups (Massachusetts Institute of Technology Press, Cambridge, Mass., 1963).

[10]See the discussion of the so-called "Transverse Optical Pumping Experiments" on gases by C. Cohen-Tannoudji and A. Kastler, in Progress in Optics, edited by E. Wolf (North-Holland Publishing Co., Amsterdam, The Netherlands, 1966), Vol. 5, p. 33.

[11]E. Adachi, J. Phys. Chem. Solids 30, 776 (1969).

[12]M. A. Habegger and H. Y. Fan, Phys. Rev. Letters 72, 99 (1964).

CRYSTAL STRUCTURE OF GAMMA NITROGEN*

R. L. Mills and A. F. Schuch

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

(Received 13 October 1969)

We have determined by x-ray diffreaction that high-pressure gamma nitrogen is tetragonal with two molecules per unit cell in special position f of space group $P4_2/mnm$. At an average pressure and temperature of 4015 ± 145 atm and 20.5 ± 1.7 K, respectively, the unit cell dimensions are $a = 3.957$ Å and $c = 5.109$ Å, giving a molar volume of 24.09 cm^3 which is in good agreement with the value 24.05 cm^3 taken from piston-displacement measurements.

Solid nitrogen is known to form three modifications; the α phase, which is cubic and exists below 35.6 K at vapor pressure; the β phase, which is hexagonal and extends from 35.6 K up to the melting curve; and the recently discovered γ phase,[1,2] which exists above 3500 atm at low temperature, and the boundary lines of which form a triple point with the other two phases at 44.5 K and 4650 atm.

The experimental difficulties in carrying out diffraction experiments on solidified gases at high pressure are considerable and no previous attempt has been made to determine the crystal structure of γ nitrogen. Such a determination is of interest in showing how N_2 molecules, which are already closely packed in the α and β phases, can be compacted further under high pressure. A knowledge of the structure is also basic to the interpretation of any future studies[3] of the properties of γ N_2.

We have determined by means of x-ray diffraction the crystal structure of γ N_2. A special technique was used to fill the sample holder in which a measured amount of hcp N_2 was first formed near vapor pressure and cooled to 50 K. The pressure was then increased to around 4500 atm with fluid He and the temperature was lowered to about 20 K. During this latter process, the He