

would be more pronounced than in the almost free electron case of copper.

As has already been stated, increasing the temperature increases thermal vibration and expands the lattice both of which decrease energies between bands. Since the energy gap is narrowed, the behavior should be more electronic. The narrowing of the gap and the consequent greater electronic behavior are in accord with Hall data. Such behavior would tend to make the Fermi surface more spherical.

Obviously this has significance for optical behavior. In the model presented above, the change in the gap energy with temperature will be observed in the shift of the reflectivity edge.

The following conclusions may be drawn: (1) the reflectivity edge in β -brass, as in silver, is plasmalike in character, (2) the position of the plasma frequency and the closely associated reflectivity minimum is strongly dependent upon the energy range of the interband transition, (3) the strong temperature effects in β -brass and in silver compared to copper and gold are probably due to the nature of the plasma-interband coupling in the former compared with absorption effects only in the latter, (4) the relation of these reflectivity curves to the Debye temperature is not clear.

Much remains to be done in clarifying the exact nature of the temperature effect and in making quanti-

tative calculations. A theoretical and experimental research program is continuing in this laboratory.

Note added in proof. Ehrenreich and Philipp³⁴ have recently examined the optical properties of silver and copper in terms of free electron effects, interband transitions, and collective oscillations. They have related the plasma resonances to characteristic energy losses and have identified interband transitions with the aid of recent band calculations. Their discussion is very important to the understanding of the optically similar β -brass.

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³⁴H. Ehrenreich and H. R. Philipp, Phys. Rev. (to be published).

Interband Transitions and Maser Action

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The possibility of using interband transitions to achieve maser action is considered. The criterion for maser action is presented in a way which allows the most direct use of optical absorption data. The absorption constant for interband transitions, which is negative corresponding to induced emission when a population exists, is related to the normal absorption constant for direct, indirect, and indirect exciton transitions. Using available absorption data, it is shown that in Ge maser action, using either the indirect or indirect exciton transitions, would be prevented by absorption due to free carriers. In GaAs, or other materials with a direct band gap, however, it is entirely possible that maser action could be achieved.

SINCE the initial operation of the ruby maser, there has been considerable speculation concerning the possibility of observing maser action in semiconductors such as Ge and Si. These semiconductors, as well as several of the III-IV and II-VI intermetallic compounds have several interesting features. First, it is possible to prepare relatively pure, homogeneous, single crystals, with reasonably good optical properties. Secondly, it is possible in semiconductors to excite electrons by injection or by avalanche breakdown techniques rather than by optical pumping. Finally, the band structure and optical properties are sufficiently well

known, such that it should be possible to theoretically decide whether or not certain transitions can give rise to maser action.

Opposing these advantages are several characteristics which are usually not present in current laser materials. First, free-carrier absorption of emitted light is possible because of the continuous density of levels to which the carriers may be excited. Free-carrier absorption is, in fact, a sufficiently important dissipative mechanism for photons, such as to overshadow the losses suffered at imperfectly reflecting end surfaces. Secondly, nonradiative recombination through localized

recombination centers almost invariably dominates the lifetimes of hole-electron pairs.¹ The result of this is that much greater pumping rates are required to establish a given nonequilibrium carrier distribution than would be necessary if nonradiative processes were not important. There is some possibility, however, that for rather large nonequilibrium populations the recombination rate through localized levels might saturate, giving, thereby, a longer lifetime for excess carriers. Also, recombination lifetimes of semiconductors vary by orders of magnitude from one substance to another or even between different specimens of the same material or the same specimen at different temperatures. It may be possible to find a semiconductor, particularly a large-gap material, wherein nonradiative recombination is not such a formidable obstacle. In any case, in the following considerations we shall try to establish whether or not maser action would occur in semiconductors given certain idealized carrier distributions, but we shall not try to decide whether or not such carrier distributions could be obtained.

Maser action occurs when the photon field of a given electromagnetic mode induces a greater amount of photon emission than it does photon absorption. The photon population builds up until it is limited by the finite rate with which excited electronic states are produced. Conditions for maser action have been obtained by Combrisson, Honig, and Townes² for the case of a single pair of levels radiating into a Lorentzian-shaped line. We shall consider in this report the case of interband transitions for which case continuous absorption spectra exist. We will formulate the criterion for maser action in a way that will allow the direct use of optical absorption data rather than presenting the criterion in terms of the matrix elements for the transitions involved, which are at best difficult to obtain.

Consider an electromagnetic mode propagating in a direction perpendicular to the reflecting end surfaces of an optical maser structure. The time rate of change of N , the number of photons in the mode, will be given by a sum of three terms:

$$dN/dt = (dN/dt)_S + (dN/dt)_{FC} + (dN/dt)_I. \quad (1)$$

The first two terms $(dN/dt)_S$ and $(dN/dt)_{FC}$ correspond to a decrease of the photon population due to reflectivity losses at the surfaces and absorption in the bulk, respectively. $(dN/dt)_I$ is the interband transition rate and is positive, corresponding to photon emission, in the case where one has a true population inversion. In order for maser action to occur, a positive $(dN/dt)_I$ must be able to overcome the photon losses represented by $(dN/dt)_S$ and $(dN/dt)_{FC}$. We can give the rate of

loss of photons at the surface easily enough as

$$(dN/dt)_S \cong \delta N / \delta t = (1-R)N / (ln_0/c) \\ = (1-R)Nc/n_0l, \quad (2)$$

where R is the reflectivity of the end surfaces and l the distance between them, n_0 is the index of refraction, and c is the velocity of light.

It will be more convenient for the purposes of directly using available absorption data, to relate dN/dt to a generalized absorption constant K which will again be a sum of terms analogous to those in dN/dt . Using $K = -(n_0/c)(1/N)dN/dt$, we obtain

$$K = (1-R)/l + K_{FC} + K_I. \quad (3)$$

$(1-R)/l$ represents the average loss per unit path length due to reflectivity losses at the surfaces and might more accurately be represented by $-\ln R/l$; however, since R is usually close to unity, little error will result from our present expression. K_{FC} is the empirical free-carrier absorption constant corresponding to the number of holes and electrons in the substance under consideration. One must take care to obtain K_{FC} for the correct conditions of impurity scattering, temperature, and wavelength in the sample. K_I is the absorption constant for interband transition and is negative when a population inversion exists. $-K_I$ then becomes a photon amplification constant. If $-K_I$ is greater than $K_S + K_{FC}$, then the photon population will increase with time or with distance traveled by the mode and stimulated emission will be observed. In the next section we shall show how one may obtain K_I for an inverted distribution when the normal interband absorption is known.

RADIATION FROM POPULATION INVERSIONS

Population inversions may be obtained in several ways. The most straight forward inversion is obtained by having a greater fraction of filled states at some excited energy (i.e., conduction band) than one has at a lower energy (valence band). This is the only type of inversion that one can have for a direct (phononless) transition.

When direct radiative recombination is not allowed, as in Ge or Si, and recombination must proceed via indirect transitions, the population to be inverted is a combination of the electron and phonon populations. For the case where recombination involves phonon emission, the excited state involves a conduction band (or exciton) electron, which in the ground state is a valence band electron plus a phonon of wave vector approximately equal to that of a conduction minimum. At low temperatures there will be virtually no phonons of this type present in the lattice and, therefore, even the presence of a few excited electrons and holes will constitute a population inversion.

Since it is our object to show how one may use ab-

¹ W. P. Dumke, Phys. Rev. **105**, 139 (1957).

² J. Combrisson, A. Honig, and C. H. Townes, Compt. rend **242**, 2451 (1956).

sorption data to predict induced emission probabilities, we shall briefly sketch the theory of interband optical transitions. For direct transitions one need only consider the electromagnetic interaction Hamiltonian $H' = (e/mc)\mathbf{A} \cdot \mathbf{P}$ where \mathbf{A} is the vector potential of an electromagnetic mode and \mathbf{P} is the momentum operator for electrons. The matrix elements of \mathbf{P} connect states of the same momentum in bands of different parity. The matrix elements of \mathbf{A} connect the initial state of the electromagnetic field with final states which have one more or one less photon. The probability that a photon will be absorbed as an electron is excited to the conduction band is proportional to N , the initial number of photons and the probability of photon emission as the electron recombines is proportional to $N+1$. We refer to that part of the emission probability that is proportional to N as the induced emission probability and the part proportional to 1 as the spontaneous emission probability. The transition probabilities for induced photon emission or absorption are equal.

Direct Transitions

The intrinsic band-to-band absorption spectrum is measured in materials which essentially have completely filled valence bands and completely empty conduction bands. For direct transitions³ the interband absorption constant K_I has a photon energy dependence near the band edge E_g given by $K_I = A(\hbar\omega - E_g)^{1/2}$. If the electron population were inverted such that the conduction band was filled and the valence band empty, we would have photon emission instead of absorption. The propagating population of photons would increase exponentially with a spatial rate given by $-K_I = A(\hbar\omega - E_g)^{1/2}$, since the photons present would induce the emission of other photons. If the valence and conduction band masses were m_v and m_c , respectively, and the states were filled to an energy $[(1/m_c)/(1/m_v + 1/m_c)]\Delta E$ in the conduction band, and empty (filled with holes) to an energy $[(1/m_v)/(1/m_v + 1/m_c)]\Delta E$ in the valence band we would find that the photon amplification (absorption) constant would be

$$\begin{aligned} -K_I &= A(\hbar\omega - E_g)^{1/2} \quad \text{for } E_g < \hbar\omega < E_g + \Delta E, \\ \text{and} \quad K_I &= A(\hbar\omega - E_g)^{1/2} \quad \text{for } \hbar\omega > E_g + \Delta E. \end{aligned} \quad (4)$$

In practice it is sometimes difficult to get enough light through anything but the thinnest samples when direct transitions occur at the absorption edge. It is, therefore, not always possible to experimentally determine A . However, if the carrier masses are known, particularly m_c , it is possible to estimate A with reasonable accuracy.

³ J. Bardeen, F. J. Blatt, and L. H. Hall, *Proceedings of the Atlantic City Photoconductivity Conference, 1954* (John Wiley & Sons, Inc., New York, 1956).

Indirect Transitions

When the conduction and valence band extrema are not at the same point of the Brillouin zone, optical transitions must be accompanied by the emission or absorption of a phonon in order to conserve momentum. Such indirect transitions give rise to a considerably weaker absorption than do direct transitions. The energy dependence of the absorption spectrum is also different since the momentum of the final electronic state is not determined by the initial state as in direct transitions.

The indirect absorption constant can be described by a sum of terms of the form³

$$K_I = B_i [N_i(\hbar\omega + k\theta_i - E_g)^2 + (N_i + 1) \times (\hbar\omega - k\theta_i - E_g)^2], \quad (5)$$

where N_i is the average number of phonons of energy $k\theta_i$ in modes of the i th vibrational branch. (Strictly speaking, there should be different values of B_i for phonon emission denominators in the second-order transition probabilities will be slightly different in these two cases.) At low temperatures, only the process in which a phonon is emitted can occur and the absorption threshold occurs at $\hbar\omega = E_g + k\theta_i$. Similarly, in indirect emission spectra at low temperatures, only processes in which phonons are emitted are observed. These processes occur at a threshold given by $\hbar\omega = E_g - k\theta_i$. The low-temperature photon emission and absorption processes are not the inverses of each other since both involve phonon emission and have different thresholds. The most important result of this is that photons emitted at low temperatures will not be reabsorbed in an interband transition. This is another way of looking at the population inversion provided by the lattice vibrations.

At low temperatures ($N_i \cong 0$), the indirect absorption due to the i th branch of the lattice vibrations is given by $K = B_i \xi^2$, where $\xi = \hbar\omega - k\theta_i - E_g$. All of the states up to an energy ξ in both the valence and conduction bands contribute to the absorption. If we consider an electron distribution for which the valence band states are empty up to a valence band energy ΔE , and the conduction band states are filled up to the same ΔE , then we will obtain a photon amplification constant given by

$$\begin{aligned} -K_I &= B_i \xi^2 \quad \text{for } 0 \leq \xi \leq \Delta E, \\ -K_I &= F(\xi) \quad \text{for } \Delta E \leq \xi \leq 2\Delta E, \end{aligned} \quad (6)$$

where $F(\xi)$ is a monotonically decreasing function of ξ which varies between values of $B_i \Delta E^2$ at $\xi = \Delta E$ and 0 at $\xi = 2\Delta E$. The maximum rate of increase of the photon population occurs at $\xi = \Delta E$.

Indirect Exciton Transitions

It is convenient to think of the formation or annihilation of excitons as an interband transition. The

electron and hole in the exciton are required to move with the same velocity, but otherwise, assuming that their mutual separation is large compared to unit cell dimensions, the electron and hole behave as though they were moving in their respective bands. The motion of the electron and hole requires two masses for its description. With regard to each other, the particles move with their reduced effective mass, but the mass describing the motion of their center of mass is the sum of the electron and hole effective mass. The translational mass of the exciton is the one entering into the density of states in the exciton band.

If the substance containing the exciton has an indirect band edge, then phonon absorption or emission will still be necessary for exciton annihilation or creation. The threshold for these transitions is lower than that of indirect transitions by just the binding energy of the excitons, and since the electron and hole must have the same velocity, the absorption constant, at low temperatures, is of the form⁴

$$K_I = C_i(\hbar\omega + E_B - k\theta_i - E_g)^{1/2},$$

where E_B is the exciton binding energy.

If there is exactly one exciton in each state of the exciton band we will obtain an analogous photon amplification constant given by

$$-K_I = C_i(\hbar\omega + E_B + k\theta_i - E_g)^{1/2}.$$

If the distribution function for excitons was instead given by $f_{\text{ex}} = ae^{-E_{\text{ex}}/kT}$, where E_{ex} is the translational energy in the exciton band, then $-K_I$ will be given by

$$-K_I = aC_i(\hbar\omega + E_B + k\theta_i - E_g)^{1/2} \times \exp\left(-\frac{\hbar\omega + E_B + k\theta_i - E_g}{kT}\right), \quad (7)$$

which has a maximum value of $-K_I = 0.43aC_i(kT)^{1/2}$ at $\hbar\omega + E_B + k\theta_i - E_g = kT/2$.

It would be possible to have more than one exciton in any band state, since they obey Bose statistics; however, the maximum density of excitons is limited by the finite volume each of them occupies.

FREE CARRIER ABSORPTION

Although it is usually not considered to be a very strong mechanism for the absorption of radiation close to band-gap energies, free-carrier absorption is likely to be the most important photon loss mechanism in the materials under consideration. While we can make the effect of end losses less in a maser geometry by improving the reflectivity or using a longer sample, we cannot alter the free-carrier absorption without also affecting the photon emission characteristics of the material. In addition, very long (~ 10 cm) photon mean free paths are required for maser action.

Absorption by free carriers consists of indirect transi-

tions to a state in the same band which is approximately a photon energy away from the band bottom. It is of approximately the same magnitude for direct and indirect band-gap materials. Phonon scattering is usually required in order to conserve over-all momentum in the transition. Impurities are relatively ineffective in supplying the necessary momentum, since the amplitudes of the Fourier components of the impurity potential corresponding to large momentum changes are very small. For very high doping, however, it is observed that impurity scattering does enhance the free-carrier absorption.

Free-carrier absorption decreases with temperature as the lattice vibrations become less excited, but because relatively high wave number modes are involved, there is little temperature dependence of free-carrier absorption at low temperatures (below 100°K).

Excitons are expected to have cross sections for free carrier absorption given by the sum of cross sections of the electron and hole as long as the photon energy is much larger than the exciton binding energy. This is supported by observations that the cross section of electrons is the same whether they are in donor states or ionized.⁵

The absorption constant for the free carriers will be given simply by

$$K_{FC} = n\sigma_n + p\sigma_p,$$

where σ_n and σ_p are the cross sections of free electrons and holes for photon absorption at the appropriate wavelength, temperature, and crystal purity, and n and p are the total number of free (or nearly free) electrons and holes per unit volume, including those in excitons and shallow impurity states.

APPLICATION TO Ge AND GaAs

We shall now apply the above method to several cases for which detailed data on the absorption spectrum and the density of electronic states exist. The idealized carrier distributions we shall assume may not always be obtainable, but any error they introduce will prejudice the case toward maser action.

The criterion of maser action (a negative over-all absorption constant) can be simplified somewhat if we eliminate K_S under the assumption that K_I and K_{FC} are much larger quantities. K_S may indeed be made very small. For a 2-cm rod with $R=0.99$, we calculate that $K_S=0.005 \text{ cm}^{-1}$.

The available data on free carrier absorption are for higher doping than we are really interested in; however, we believe the cross sections available from the literature are probably accurate to roughly 25%.

Indirect Transitions in Ge

In this case we shall assume our valence and conduction band to be full (inverted) up to an energy ΔE .

⁴ R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

⁵ W. Spitzer and H. Y. Fan, Phys. Rev. **108**, 268 (1957).

Since $-K_I \propto (\Delta E)^2 \propto (n \text{ or } p)^{4/3}$ whereas $K_{FC} \propto n \text{ or } p$, the best chance of observing maser action will occur for large carrier concentrations. For the strongest indirect transition in Ge,⁶ the one involving a 320° phonon, $B_{320} \sim 2400 \text{ cm}^{-1} \text{ eV}^{-2}$. If we assume $\Delta E = 0.1 \text{ eV}$ corresponding to $n = 1.9 \times 10^{18} \text{ cm}^{-3}$ and $p = 1.0 \times 10^{18} \text{ cm}^{-3}$, we find $-K_I = 0.24 \text{ cm}^{-1}$. The cross sections near the absorption edge for free-carrier absorption in Ge are $\sigma_n = 0.3 \cdot 10^{-17} \text{ cm}^2$ and $\sigma_p = 0.15 \cdot 10^{-17} \text{ cm}^2$.^{7,8} For the above carrier concentrations $K_{FC} = \sim 7 \text{ cm}^{-1}$, which is 30 times too large to obtain maser action.

Si is even a more unlikely candidate, since the cross sections for free-carrier absorption are an order of magnitude larger than in Ge.

Indirect Exciton Recombination in Ge

The exciton effective mass corresponding to one conduction valley⁹ in Ge is given by

$$m_{\text{ex}} = m_v + m_c \cong 0.33m \\ + (0.08, 0.08, 1.58)m \cong (0.4, 0.4, 1.9)m$$

assuming an isotropic effective mass of $0.33m$ for the hole. With this effective mass, the density of states in the exciton band is 5.5 times the density of states in the conduction band.

Consider now that we have 10^{16} cm^{-3} excitons at 4.2°K. For this concentration the exciton distribution will be approximately

$$f_{\text{ex}} = 0.105 e^{-E_{\text{ex}}/kT}.$$

If we consider the transition involving the 320°K phonon for which⁶ $C_i = 11 \text{ cm}^{-1} \text{ eV}^{-1/2}$, the maximum value of the amplification constant $-K_I$ is given by $-K_I = 0.43 \times 0.105 C (kT)^{1/2} = 0.0094 \text{ cm}^{-1}$. For the 10^{16} cm^{-3} electrons and 10^{16} cm^{-3} holes which the excitons contain the free-carrier absorption is $K_{FC} = 10^{16} (\sigma_n + \sigma_p) = 0.045 \text{ cm}^{-1}$.

We therefore see that free-carrier absorption will prevent maser action in this case.

Note added in proof. G. Lasher has independently concluded (private communication), from the radiative lifetime of excitons in Ge and data on free carrier absorption, that a Ge exciton laser would not be feasible.

It may be possible that by going to temperatures of less than 1°K maser action could be obtained, since such low temperatures would concentrate the excitons within a smaller energy range; however, there is some experimental evidence⁶ that the exciton states have a width of several times 10^{-4} eV which width is probably temperature independent.

Direct Radiative Recombination

Consider GaAs in which, say, 10^{16} cm^{-3} electrons and 10^{16} cm^{-3} holes lie degenerately close to the band edges. (This distribution could be imagined to exist at some instant of time if the thermalization time of electrons and holes is considerably smaller than the recombination time.) The states in the conduction band will be filled to an energy 0.0023 eV from the conduction band edge and the heavy holes to an energy 0.0004 eV from the valence band edge. Both bands will have essentially the same volume in k space filled with carriers, since almost no holes will go into the light-hole band.

Photon amplification due to induced direct transitions will be a maximum for $\hbar\omega = E_g + 0.0027 \text{ eV}$. For GaAs the value of A in Eq. (4), taking into account only transitions between the heavy hole and conduction bands, can be estimated¹⁰ to be approximately $6000 \text{ cm}^{-1} \text{ eV}^{-1/2}$. The photon amplification constant will, therefore, be

$$-K_I = A (\hbar\omega - E_g) = 300 \text{ cm}^{-1}.$$

The free-carrier absorption constant can be calculated if we assume the absorption cross section of holes to be equal to the known cross section for electrons,¹¹ approximately $0.5 \times 10^{-17} \text{ cm}^2$. For 10^{16} electrons and holes we obtain $K_{FC} = 0.1 \text{ cm}^{-1}$. Clearly then, under the conditions we have described, maser action should occur in GaAs. Because the photon amplification constant is so large, it would be possible to tolerate several orders of magnitude more holes in GaAs, so that the temperature necessary for the hole distribution to remain degenerate would not be so low.

At present, it is not clear whether or not one would obtain anything like typical maser action from a device utilizing direct transitions as in GaAs. The feature that may be lacking is the possibility of mode selection. For the case we have considered, light traveling in any direction, as long as it can travel $\sim 10^{-2} \text{ cm}$, will be strongly amplified. What could result is a device exhibiting a more or less isotropic induced emission of light over a narrow band of width roughly equal to the energy to which the conduction band is full.

It can be argued, however, that many excited electromagnetic modes would almost immediately depopulate the excited electronic levels and in fact, that an electron population which gives rise to such strong maser action over so many modes could not be built up in the first place. What is most probable is that any further buildup in the electron population is suppressed when the first electromagnetic modes become excited, and that these modes are the one selected by the geometrical design of the maser. There is considerable hope then that one of the direct-gap semiconductors such as InSb, GaSb, GaAs, etc., could make a maser with the usual mode selection properties and perhaps the additional features of excitation by injection.

¹⁰ W. P. Dumke (unpublished).

¹¹ W. G. Spitzer and J. M. Whelan, Phys. Rev. **114**, 59 (1959).

⁶ G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **108**, 1377 (1957).

⁷ J. Pankove (private communication). Contains absorption data on n -type Ge at 4°K.

⁸ R. Newman and W. W. Tyler, Phys. Rev. **105**, 885 (1957); gives p -type Ge cross sections at 77°K for 0.7-eV photons.

⁹ G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).