Plasma Frequency as a Test of Intervalley Transfer in the Gunn Effect*

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We propose a test whereby the intervalley transfer of electrons in semiconductors under the influence of a high electric field can be determined. The same experiment can be used also to determine the electron temperature. The present test is based on the fact that as the transfer occurs, the plasma frequency of the electrons undergoes an appreciable change because the masses of the different valleys differ considerably.

I. INTRODUCTION

It was found by Gunn[1] that coherent microwave oscillations occur in n-type GaAs and some other III-V semiconductors when the static electric field exceeds a certain threshold value dependent on various properties of the sample. Kroemer[2] interpreted this effect in terms of the intervalley transfer mechanism discussed earlier by Ridley and Watkins,[3] i.e., the electric field causes the temperature of the electrons to rise and thus a large fraction of the electrons is transferred from the central valley to the low-mobility secondary valleys. This is now the accepted interpretation.

A direct test of this interpretation was made by Hutson *et al.*,[4] and Allen *et al.*[5] These workers reduced the energy gap between the central and secondary valleys by pressure and composition, respectively. It was found that the threshold field varies in a manner compatible with the transfer model.

In this paper we propose another test of the transfer model; namely, a measurement of the plasma frequency of the free carriers versus the static electric field. This test has the following advantages. (1) It is a direct measure of the actual transfer mechanism as the field varies from zero to the threshold. This can be seen from Eq. (14), below, which shows that the plasma frequency depends only on the concentrations in the various valleys (the effective masses are usually known reliably). This is to be compared with the previous tests[4,5] where only the dependence of the threshold field on the energy gap is studied. These tests give no information on what happens below the threshold field. (2) The present test, if realized, should settle the question of how much actual transfer occurs as a function of the field. The theory presented here, which follows McCumber and Chynoweth,[6] suggests a gradual transfer long before the threshold field. On the other hand, Conwell and Vassel[7] obtain from their calculations a sudden onset of transfer slightly before the threshold field is reached. (These two results are compared in Fig. 1.) Therefore it seems worthwhile to settle this question experimentally. (3) The present test can serve to determine the electron temperature from plasma frequency measurement alone [see Eqs. (14) and (28)] since other parameters are known. In this way we have a test of the applicability of a single temperature for all valleys as assumed by McCumber and Chynoweth.[6]

We now state the important advantages that the plasma measurements have over mobility measurements in determining intervalley transfer below threshold. As stated above, the plasma frequency depends solely, and in a simple way, on the mass parameters of the valleys. Furthermore, the masses are independent of the applied field. On the other hand, the mobilities of the individual valleys are field-dependent (although for simplicity, we take it to be field-independent in what follows) and in a complicated manner. To complicate matters, the electrons in the primary valley (see Sec. II and Fig. 2) with energies larger than the separation energy Δ have a mobility closer to that of the secondary valley than that of primary valley [see discussion following Eq. (17)]. In summary we can state that although we present here a calculation of the plasma frequency, it is our main contention that once this plasma frequency is experimentally determined, the intervalley transfer can be found without any theory at all by using Eq. (14).

One can also use mobility and Hall-effect measurements to determine intervalley transfer[8,9] but, as we pointed out above, one cannot make a one-to-one correspondence between the mobilities and the valleys, i.e., masses. In other words, both plasma and mobility measurements are useful but they do not measure the same thing.[9]

In Sec. II, the basic electromagnetic theory of the longitudinal plasma mode is presented. In Sec. III, we calculate the high-frequency electrical conductivity and hence the plasma frequency for a two-valley model of a semiconductor. Section IV contains a calculation of the partial concentrations in the two valleys. These con-

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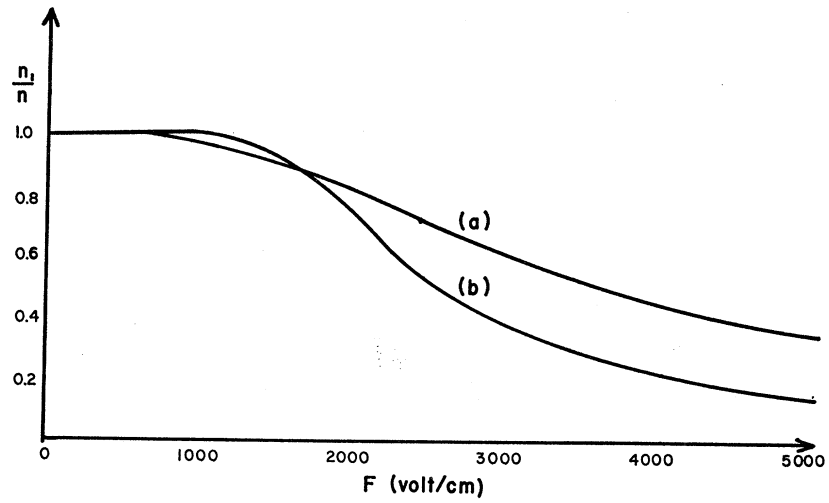

FIG. 1. Concentration in the central valley, n_1/n, in GaAs versus the field F. (a) Present Theory. (b) Theory of Cornwell and Vassel.

centrations are needed for the evaluation of the plasma frequency. In Sec. V, we discuss some experimental procedures that can be used to measure the plasma frequency. Section VI contains an application of the theory to two representative semiconductors, GaAs and GaSb. Determination of the concentrations of the valleys and the temperature of the electrons directly from the plasma frequency is given in Sec. VII. Section VIII contains some concluding remarks.

II. ELECTROMAGNETIC THEORY AND PLASMA FREQUENCY

We will begin our discussion by a very brief resume of the band structure of many-valley semiconductors.

Figure 2 shows the essential features of the conduction bands of those many-valley semiconductors[10] which display the Gunn effect. The lower valley (primary) has a much smaller mass than the higher valley (secondary). The primary and secondary valleys are placed at the center and the edge of the Brillouin zone (the secondary valleys being along the [111] direction). This is not an essential feature for the Gunn effect. However, if the secondary valleys do not occur at the center of the zone then the usual cubic symmetry guarantees the existence of equivalent secondary valleys in other equivalent directions; e.g., Fig. 2 implies the existence of 8 half secondary valleys. This multiplicity of the secondary valleys aids the transfer process considerably and thus favors the appearance of the Gunn effect. We remark that the exact location of the secondary valleys is not important and the specific features of Fig. 2 are chosen for illustration. Finally, we will assume the valleys to be spherical with parabolic dependence on k; i.e., we assume the existence of isotropic effect masses. Let the effective masses be m_1 and m_2 and the partial concentrations be n_1 and n_2 (subscripts 1 and 2 refer to primary and secondary valleys, respectively).

[10] For much information on the band structures of the III-V semiconductors see J. Appl. Phys. Suppl. 32, 2094 (1961).

The electromagnetic (EM) fields in a conducting medium satisfy the following Maxwell equations

$$\nabla\times\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t}, \tag{1}$$

and

$$\nabla\times\mathbf{H}=\frac{4\pi}{c}\sigma\mathbf{E}+\frac{\epsilon_L}{c}\frac{\partial\mathbf{E}}{\partial t}, \tag{2}$$

where σ is the electrical conductivity, and ϵ_L is the dielectric constant of the lattice. Taking the curl of (1) and substituting from (2), we obtain

$$\nabla\times(\nabla\times\mathbf{E})=-\frac{\epsilon_L}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}-\frac{4\pi}{c^2}\sigma\frac{\partial\mathbf{E}}{\partial t}. \tag{3}$$

We are interested in the longitudinal plane-wave solution of (3). Substituting $\mathbf{E}$ of the form

$$\mathbf{E}=\hat{q}E_0e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}, \tag{4}$$

where $\hat{q}$ is a unit vector in the direction of $\mathbf{q}$, we obtain

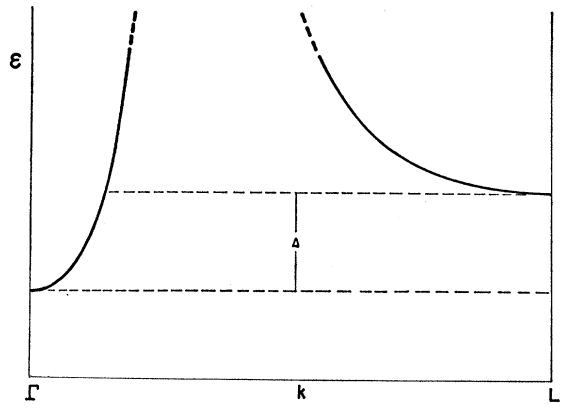

FIG. 2. Conduction band of a two-valley semiconductor which show the Gunn effect. The lower and upper valleys are at the center and edge (along the [111] direction) of the Brillouin zone. The upper valley has a much larger mass than the lower valley.

the following secular equation

$$\omega=-i(4\pi/\epsilon_L)\sigma. \tag{5}$$

At the frequency of interest here, σ is a function of ω. Any root of (5) is called a longitudinal plasma frequency ω_p. We turn now to the calculation of σ.

III. HIGH-FREQUENCY ELECTRICAL CONDUCTIVITY

We use the Boltzmann relaxation equation[11] BRE in order to calculate σ. For an electron in the ith valley the BRE is

$$\frac{\partial f}{\partial t}=-\frac{\hbar\mathbf{k}}{m_i}\cdot\frac{\partial f}{\partial \mathbf{r}}-\frac{e\mathbf{E}}{\hbar}\cdot\frac{\partial f}{\partial \mathbf{k}}-\frac{f-f^0}{\tau_i}, \tag{6}$$

where f is the distribution function, f^0 is the distribution function in the absence of the field $\mathbf{E}$, and τ_i is the relaxation time for the ith valley. There is a standard method[12] for solving (6) for small $\mathbf{E}$. We assume

$$f=f^0+f', \tag{7}$$

where f' is a small deviation. To linear terms in E, $f'\sim e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$. Substituting (7) into (6) and retaining only linear terms, we obtain

$$f'=-\frac{e\hbar\tau_i(\mathbf{E}\cdot\mathbf{k})\partial f^0/\partial\epsilon}{m_i[1-\tau_i(\omega-\mathbf{q}\cdot\mathbf{v}_i)]}, \tag{8}$$

where v_i is the group velocity of the electron. Equation (8) can be simplified for semiconductors where $\mathbf{q}\cdot\mathbf{v}_i\ll\omega$ in the frequency range of interest. Therefore, to a good approximation

$$f'=\frac{e\hbar\tau_i}{m_i(1-i\omega\tau_i)}(\mathbf{E}\cdot\mathbf{k})\left(\frac{\partial f^0}{\partial\epsilon}\right). \tag{9}$$

The electrical conductivity of the ith valley is

$$\sigma_i=\frac{\mathbf{J}}{\mathbf{E}}=\frac{e\int\mathbf{v}_i f g_i(\epsilon)d\epsilon}{\mathbf{E}}, \tag{10}$$

where $\mathbf{J}$ is the current density, and $g_i(\epsilon)$ is the density-of-states function for the ith valley. To evaluate σ_i, we substitute for f from Eqs. (7) and (9). The resulting integral is simple to perform if τ_i is independent of ϵ. With this assumption, the result is

$$\sigma_i=\left(\frac{n_i e^2\tau_i}{m_i}\frac{1+i\omega\tau_i}{1+\omega^2\tau_i^2}\right). \tag{11}$$

The assumption of constant relaxation time cannot be rigorously justified; however, its energy dependence is not critically relevant to the transfer mechanism under discussion here.[6]

The inequality $\omega\tau_i\gg1$ is important for the observation of resonance absorption. It will be shown in Sec. VI that in the frequency range of interest this inequality can be well satisfied. When $\omega\tau_i\gg1$, then Eq. (11) reduces to

$$\sigma_i=in_i e^2/m_i\omega. \tag{12}$$

The total conductivity σ is given by

$$\sigma=\sum_{i=1}^{2}\sigma_i=i\sum_{i=1}^{2}\frac{e^2 n_i}{m_i\omega}. \tag{13}$$

Substituting (13) into (5), we obtain the following solution for the plasma frequency:

$$\omega_p=\left[\frac{4\pi e^2}{\epsilon_L}\left(\frac{n_1}{m_1}+\frac{n_2}{m_2}\right)\right]. \tag{14}$$

IV. PARTIAL CONCENTRATIONS AT HIGH STATIC ELECTRIC FIELD

One effect of the static field F is to raise the effective temperature T_e of the electron system, and hence to transfer electrons from the lower to the upper valley. We will now calculate the partial concentrations as a function of the field F. The basic idea of the method used here is that the rate of energy gained by the electron from the field F is equal to that lost to the lattice.[6] This energy conservation we will write in the form

$$eF\langle v_d\rangle=-[\langle E(T_e)\rangle-\langle E(T)\rangle]/\tau_\theta, \tag{15}$$

where $\langle v_d\rangle$ is the average drift velocity. The quantities $\langle E(T_e)\rangle$, and $\langle E(T)\rangle$ are the average energy of the electron at temperature T_e and lattice temperature T, respectively, and τ_θ is an energy relaxation time which is of the same order of magnitude as the collision times.

It is shown in the Appendix [see Eq. (A9)] that

$$\langle E(T)\rangle=\tfrac{3}{2}k_BT+\Delta\frac{\alpha e^{-\Delta/k_BT}}{1+\alpha e^{-\Delta/k_BT}}, \tag{16}$$

where $\alpha=(N_2/N_1)(m_2/m_1)^{3/2}$, Δ is the energy gap between the valleys, and N_1 and N_2 are the number of equivalent primary and secondary valleys, respectively. $\langle E(T_e)\rangle$ has the same form as (16) with T_e replacing T.

The average drift velocity $\langle v_d\rangle$ is given by

$$\langle v_d\rangle=[(n_1'/n)\mu_1+(n_2'/n)\mu_2]F, \tag{17}$$

where μ_1, μ_2 refer to the mobilities. The quantities n_1' and n_2' are concentrations of electrons with mobilities μ_1 and μ_2, respectively. According to McCumber and Chynoweth,[6] an electron in the lower valley with energy larger than Δ has mobility μ_2 rather than μ_1 because it can scatter into upper valleys and hence has a lower mobility. It is shown in the Appendix [see Eq. (A12)]

[11] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, New York, 1964), p. 179. In using the BRE, we are assuming the existence of a relaxation time.

[12] See Ref. 11, pp. 238, 239.

that

$$\frac{n_1'}{n}=\frac{1}{1+\alpha e^{-\Delta/k_BT_e}}\left[1-\frac{2}{\pi^{1/2}}\Gamma\left(\tfrac{3}{2},\frac{\Delta}{k_BT_e}\right)\right], \quad (18)$$

where we use the incomplete gamma function[13]

$$\Gamma(a,Z)=\int_Z^\infty t^{a-1}e^{-t}dt. \quad (19)$$

We also have

$$n_2'/n=1-n_1'/n. \quad (20)$$

Substituting from (16)-(20) into (15), we obtain an equation in T_e which now can be solved for as a function of F.

To calculate the plasma frequency ω_p in (14), we need n_1/n and n_2/n. For the electron system at temperature T_e, it is shown in the Appendix [see Eq. (A6)] that

$$n_1/n=(1+\alpha e^{-\Delta/k_BT_e})^{-1}. \quad (21)$$

Of course, $n_2/n=1-n_1/n$. We see that once T_e is found [from (15)-(20)], n_1/n and n_2/n can be found from (21), and ω_p calculated from (14).

V. OBSERVABILITY

We turn now to the question of experimental determination of the plasma frequency ω_p. At least two different methods can be used, i.e., the method of optical reflection and that of Raman scattering. Before discussing these methods, we will introduce the concept of the total dielectric constant which we will find convenient in discussing the above methods.

The total dielectric constant ϵ_T at long wavelengths, including both lattice and free-carrier polarizations, is given by[14]

$$\epsilon_T=\epsilon_L[1-\omega_p^2\tau/\omega(\omega\tau+i)], \quad (22)$$

where τ is the mobility collision time introduced to account for electron collision. If we write $\epsilon_T=\epsilon_1+i\epsilon_2$, we find that

$$\epsilon_1=\epsilon_L(1-\omega_p^2\tau^2/\omega^2\tau^2+1), \quad (23a)$$

and

$$\epsilon_2=\epsilon_L(\omega_p^2\tau/\omega(\omega^2\tau^2+1). \quad (23b)$$

Now we take up the optical reflection method. The reflectance of the medium for a normally incident EM wave is given by

$$R=[(\eta-1)^2+\kappa^2]/[(\eta+1)^2+\kappa^2], \quad (24)$$

where η and κ are, respectively, the real and imaginary parts of the complex refraction index.[14] These quantities are related to ϵ_1 and ϵ_2 by[14]

$$\eta=\{\tfrac{1}{2}[\epsilon_1+(\epsilon_1^2+\epsilon_2^2)^{1/2}]\}^{1/2} \quad (25a)$$

and

$$\kappa=\{\tfrac{1}{2}[-\epsilon_1+(\epsilon_1^2+\epsilon_2^2)^{1/2}]\}^{1/2}, \quad (25b)$$

It will be shown now that, if $\omega_p\tau\to\infty$ (whose validity for specific materials will be discussed below), the reflectance decreases sharply with increasing ω from $R\approx1$ to $R\approx0$ at $\omega\approx\omega_p$. There is a sharp reflection edge at the plasma frequency. We see from Eqs. (23a)-(25b) that, if $\omega_p\tau\gg1$, then $\epsilon_1\approx\epsilon_L[1-(\omega_p^2/\omega^2)]$, $\epsilon_2\approx0$, and $\kappa\approx0$. Hence for $\omega<\omega_p$, $\epsilon_1>0$, $\eta\neq0$, and $R<1$, while for $\omega>\omega_p$, $\epsilon_1>0$, $\eta\neq0$, and $R<1$. In fact R decreases to zero at $\omega=\omega_p(1-1/\epsilon_L)^{-1/2}$ and increases as ω increases further, i.e., R passes through a minimum. The decrease in R is sharp if $\epsilon_L\gg1$, as is the case for the media under consideration. We see thus that either the reflection edge or the minimum point can be used to measure ω_p experimentally. Experimental graphs illustrating this behavior of R versus ω can be found in the literature.[15]

As $\omega_p\tau$ decreases, damping sets in, the reflection edge broadens, and the minimum of R rises above zero. Both the edge and the minimum remain recognizable as long as $\omega_p\tau\gg1$ is well satisfied, although the minimum is still recognizable and usable even for $\omega_p\tau=1$. In fact, this minimum has been used extensively in practice[15] to obtain information of the same nature as ω_p.

Now we move on to a discussion of Raman scattering of an EM wave from the plasma system, a subject receiving much attention lately.[16] Rather than delve into the details of this subject here, we merely quote the results essential to our immediate interest. Raman scattering due to plasmon excitations was discussed by McWhorter.[17] Such scattering was observed[18] subsequently in GaAs by exciting the plasmons with a laser beam and observing the spectrum of the scattered light. An anti-Stoke line corresponding to $\omega+\omega_p$ was clearly observed. Of course, the sharpness of the line depends on how well the condition $\omega_p\tau\gg1$ is satisfied. Another method of measuring ω_p is to observe radiation emitted from plasmons in a foil. The plasmons can be excited by an EM field which contains the plasma frequency in its spectrum and whose electric field has a component perpendicular to the foil.[19]

VI. NUMERICAL VALUE FOR GaAs AND GaSb

Figures 3 and 4 are plots of Ω_p versus F for GaAs and GaSb (as two representative semiconductors), respec-

[13] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1964), Appl. Math. Ser. 55, p. 297.

[14] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), Sec. 4-4.

[15] J. T. Houghton and S. D. Smith, *Infra-Red Physics* (Oxford University Press, New York, 1966), Fig. 4.12.

[16] See, for example, E. Burstein, in *Dynamical Processes in Solid State Physics*, edited by R. Kubo and H. Kamimura (W. A. Benjamin, Inc., New York, 1967), p. 34.

[17] A. L. McWhorter, in *Physics of Quantum Electronics*, edited by P. L. Kelly, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Co., New York, 1966), p. 111.

[18] A. Mooradian and G. B. Wright, Phys. Rev. Letters **16**, 999 (1966). Actually the modes excited here are mixed plasmon-LO phonons but this point does not interest us here.

[19] J. Bosenberg, Phys. Letters **26A**, 74 (1967).

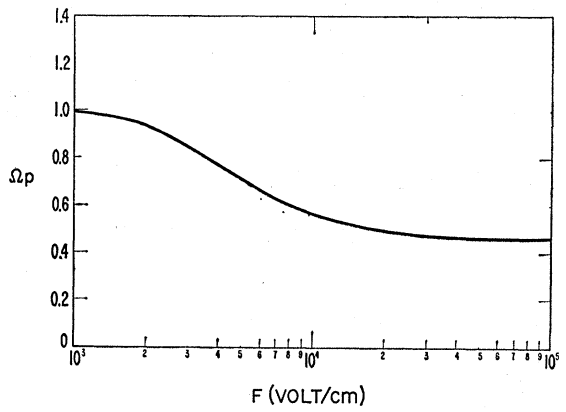

FIG. 3. Normalized plasma frequency Ω_p versus electric field F in n-type GaAs.

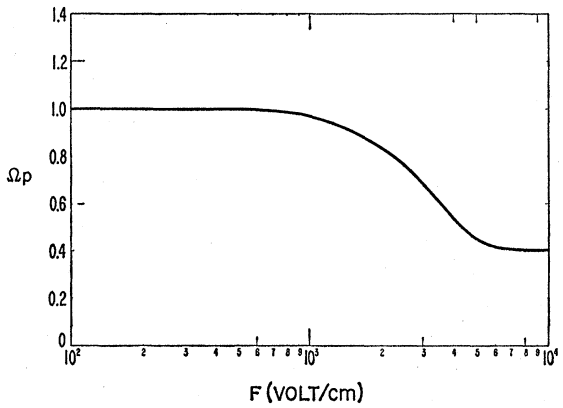

FIG. 4. Normalized plasma frequency Ω_p versus electric field F in n-type GaSb.

tively, where Ω_p is a normalized plasma frequency defined by

$$\Omega_p \approx \omega_p \left(\frac{4\pi e^2}{\epsilon_L} \frac{n}{m_1} \right)^{-1/2}, \tag{26}$$

and where ω_p is calculated according to the theory presented in Secs. II–IV. These figures show the expected decrease in ω_p as the electric field is raised and electrons are transferred to the upper valley. The parameters used in the calculations are listed in Table I. The energy relaxation time τ_θ appearing in the table is so chosen that the calculated and observed threshold fields agree for GaAs. For GaSb, τ_θ is estimated from that of GaAs and density-of-states effective masses for the two compounds (the Gunn effect has not yet been observed in GaSb but the intervalley transfer should occur nonetheless).

We now investigate the validity of the condition $\omega_p\tau \gg 1$ utilized in Sec. V. As pointed out there, τ is the mobility collision time which may be much smaller than τ_θ especially for nearly elastic collision. The subject of electron collision in a many-valley semiconductor is quite involved[20] but here we are interested only in estimating $\omega_p\tau$. We will take $\tau \approx \tau_\theta$ because at high electric field the collision is dominated by intervalley scattering which is highly inelastic.[20] Because of this fact, we expect that τ and τ_θ do not differ much from each other. Furthermore, τ can be increased markedly by lowering the lattice temperature because the scattering is due mainly to electron-phonon interaction.

Now we can easily estimate $\omega_p\tau_\theta$ for GaAs. Taking $n = 5\times10^{16}$ cm^{-3} (a typical concentration for samples showing the Gunn effect), $\epsilon_L = 12.5$, and τ_θ from the table, we find

$$\omega_p \approx (4\pi n e^2/\epsilon_L m_1)^{1/2} \approx 1.2\times10^{13} \text{ sec}^{-1};$$

therefore $\omega_p\tau_\theta \approx 80$, a figure much larger than unity. The product $\omega_p\tau_\theta$ can be increased further by lowering the lattice temperature, as we pointed out previously.

The frequency $\omega_p = 10^{13}$ sec^{-1} ($\nu \approx 1.60\times10^{12}$ cps) falls in the far infrared region of the EM spectrum. Thus measurement of ω_p by the reflection method (see Sec. V) should be possible with present-day techniques. Also, by increasing the concentration, one can displace ω_p into a more convenient region. The Raman scattering technique is also quite suitable for this frequency range, since this technique does not measure ω_p directly but as the difference between two frequencies in a well-studied region of the spectrum, e.g., the infrared region. We point out that the free-carrier concentration under discussion is of the same order of magnitude as that used in Ref. 18.

VII. CONCENTRATIONS AND ELECTRON TEMPERATURE

When ω_p is determined experimentally (see Secs. V and VI), n_1/n can be solved for from (14). The result is

$$\frac{n_1}{n} = \left(\frac{\omega_p^2}{(4\pi e^2/\epsilon_L m_1)} - 1 \right) \frac{m_2}{m_2 - m_1}. \tag{27}$$

The electron temperature can be solved for from (21) with the result

$$T_e = -\frac{\Delta}{k_B} \ln\left[\frac{1}{\alpha} \left(\frac{n}{n_1} - 1 \right) \right]. \tag{28}$$

Thus, when n_1/n is determined from (27), Eq. (28) can

[20] E. M. Conwell and M. O. Vassell, IEEE Trans. Electron Devices **ED-13**, 22 (1966). See also E. M. Conwell, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1967), Suppl. 9, Sec. V-7.

TABLE I. Transport and band parameters for GaAs and GaSb.[a]

	μ_1(cm²/V sec)	μ_2(cm²/V sec)	α	Δ(eV)	$m_1(m_0)$	$m_2(m_0)$	T(°K)	τ_θ(sec)
GaAs	5000	400	60	0.35	0.072	0.364	300	7×10^{-12}
GaSb	4000	1400	72.8	0.08	0.052	0.36	70	3.6×10^{-12}

[a] The numerical values of the parameters used here are taken from the following sources: C. Hilsum, *Physics of Semiconductors* (Academic Press Inc., New York, 1964), p. 1127; W. M. Becker *et al.*; Ref. 10; D. E. McCumber and A. G. Chynoweth; and Ref. 6 above.

be used to calculate T_e versus F. This determination of T_e is independent of the detailed dynamics of the problem.

We would like to stress, here, the importance of this determination of T_e directly from the plasma frequency measurement. When T_e is known, the partial concentrations can be calculated from (18). This information about the concentrations can be used in conjunction with conductivity measurement to shed light on the mobilities.

It should be mentioned that Fig. 3, for GaAs, is not valid beyond the threshold field because the electron distribution becomes spatially inhomogeneous; the present theory predicts a threshold field[14] of $\approx3.0\times10^3$ V/cm. On the other hand, Fig. 4, for GaSb is valid throughout because no instability is predicted[21] or observed.

VIII. CONCLUSION

We presented here what we believe to be a good test of intervalley electron transfer through plasma frequency measurements. We realize there are many shortcomings in the theory advanced here for calculating the plasma frequency. However, the existence of the plasma frequency is independent of this theory, and its measurement reflects the intervalley transfer regardless of the mechanism responsible for this transfer.

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APPENDIX

Assume that the electron system can be represented by a Maxwellian distribution with a temperature T_e. Then we may write the distribution function as

$$f(\epsilon)=e^{\epsilon_f/k_BT_e}e^{-\epsilon/k_BT_e}, \tag{A1}$$

where ϵ_f is the Fermi energy. We now have

$$n_1=\int_0^\infty f(\epsilon)g_1(\epsilon)d\epsilon$$

$$=\frac{1}{2\pi^2}\left(\frac{2m_1}{\hbar^2}\right)^{3/2}e^{\epsilon_f/k_BT_e}\int_0^\infty \epsilon^{1/2}e^{-\epsilon/k_BT_e}d\epsilon$$

$$=\frac{1}{4\pi^{3/2}}\left(\frac{2m_1k_BT_e}{\hbar^2}\right)^{3/2}e^{\epsilon_f/k_BT_e}, \tag{A2}$$

where $g_1(\epsilon)$ is the density-of-states function for the primary valley. Similarly,

$$n_2=\frac{N_2}{2\pi^2}\left(\frac{2m_2}{\hbar^2}\right)^{3/2}e^{\epsilon_f/k_BT_e}\int_0^\infty (\epsilon-\Delta)^{1/2}e^{-\epsilon/k_BT_e}d\epsilon$$

$$=\frac{N_2}{4\pi^{3/2}}\left(\frac{2m_2k_BT_e}{\hbar^2}\right)^{3/2}e^{-\Delta/k_BT_e}e^{\epsilon_f/k_BT_e}. \tag{A3}$$

The total concentration is given by

$$n=n_1+n_2. \tag{A4}$$

Substituting (A2) and (A3) into (A4), we can solve for the Fermi energy which is now given by

$$\frac{\epsilon_f}{e^{k_BT_e}}=\frac{n}{(1+\alpha e^{-\Delta/k_BT_e})}\frac{4\pi^{3/2}}{(2m_1k_BT_e/\hbar^2)^{3/2}}. \tag{A5}$$

Substituting (A5) into (A2), we obtain

$$n_1/n=(1+\alpha e^{-\Delta/k_BT_e})^{-1}, \tag{A6}$$

which is Eq. (21).

The average energy is given by

$$\langle E(T_e)\rangle=\frac{1}{n}\left[\int_0^\infty \epsilon f(\epsilon)g_1(\epsilon)d\epsilon+\int_\Delta^\infty \epsilon f(\epsilon)g_2(\epsilon)d\epsilon\right]. \tag{A7}$$

Substituting from (A1) and (A5), we obtain

$$\langle E(T_e)\rangle=\frac{2}{\pi^{1/2}(k_BT_e)^{3/2}}\left[\int_0^\infty \epsilon^{3/2}e^{-\epsilon/k_BT_e}d\epsilon\right.$$

$$\left.+\alpha\int_\Delta^\infty \epsilon(\epsilon-\Delta)^{1/2}e^{-\epsilon/k_BT_e}d\epsilon\right]\Big/(1+\alpha e^{-\Delta/k_BT_e}). \tag{A8}$$

[21] M. A. Omar (unpublished).

The first integral in (A8) can be integrated at once in terms of a gamma function.[13] The second integral can similarly be evaluated by an obvious change of variables. The result is

$$\langle E(T_e)\rangle=\tfrac{3}{2}k_BT_e+\Delta(\alpha e^{-\Delta/k_BT_e})/(1+\alpha e^{-\Delta/k_BT_e}). \quad \text{(A9)}$$

This is the equation on which (16) is based.

We now calculate n_1', the number of electrons in the lower valley whose energy is less than Δ. This is given by

$$n_1'=\int_0^{\Delta} f(\epsilon)g_1(\epsilon)d\epsilon. \quad \text{(A10)}$$

Substitution from (A1) and (A5) gives

$$n_1'=\frac{n}{1+\alpha e^{-\Delta/k_BT_e}}\frac{2}{\pi^{1/2}}\int_0^{\Delta/k_BT_e} x^{1/2}e^{-x}dx. \quad \text{(A11)}$$

The integral in (A11) can be rewritten as

$$\begin{aligned}\frac{2}{\pi^{1/2}}\int_0^{\Delta/k_BT_e} x^{1/2}e^{-x}dx &=\frac{2}{\pi^{1/2}}\int_0^{\infty} x^{1/2}e^{-x}dx-\frac{2}{\pi^{1/2}}\int_{\Delta/k_BT_e}^{\infty} x^{1/2}e^{-x}dx\\ &=1-\frac{2}{\pi^{1/2}}\int_{\Delta/k_BT_e}^{\infty} x^{1/2}e^{-x}dx\\ &=1-\frac{2}{\pi^{1/2}}\Gamma\left(\tfrac{3}{2},\frac{\Delta}{k_BT_e}\right),\end{aligned}$$

where we used the incomplete gamma function.[13] Substituting the above result in (A11) we finally obtain

$$\frac{n_1'}{n}=\frac{1}{1+\alpha e^{-\Delta/k_BT_e}}\left[1-\frac{2}{\pi^{1/2}}\Gamma\left(\tfrac{3}{2},\frac{\Delta}{k_BT_e}\right)\right]. \quad \text{(A12)}$$

This is Eq. (18) of the text.

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Raman Effect in Wurtzite- and Zinc-Blende-Type ZnS Single Crystals*

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Raman spectra of wurtzite- and zinc-blende-type ZnS single crystals were excited by a He-Ne laser (6328 Å) and an argon-ion laser (4880 Å and 5145 Å). All the Raman-active long-wavelength phonon frequencies were determined. These are (i) for the cubic modification, TO = 276 cm^{-1} and LO = 351 cm^{-1}; and (ii) for the hexagonal modification, E_2 = 72 cm^{-1}, E_2 = 286 cm^{-1}, A_1(TO) = E_1(TO) = 273 cm^{-1}, and A_1(LO) = E_1(LO) = 351 cm^{-1}. The lowest-frequency E_2 mode of the mixed crystal system $Cd_xZn_{1-x}S$ was studied as a function of x, and was found to vary monotonically. The intensity ratio of the LO to the TO band seems to be dependent on the wavelength of the exciting radiation.

I. INTRODUCTION

RAMAN spectra of several II–VI compounds, viz., ZnO, CdS, ZnSe, and ZnTe, have been reported[1–4] in recent years and have been properly assigned. Poulet, Klee, and Mathieu[5] have reported the Raman spectrum of hexagonal ZnS(2*H*) using conventional Hg-arc source excitation. This work is not complete. Firstly, it appears, in light of the present work, that the assignment given by them is not correct; secondly, they did not observe all the expected first-order Raman bands for a wurtzite-type crystal. There has also been an attempt[6] to extrapolate the position of the lowest-frequency Raman-active fundamental (E_2) of ZnS(2*H*) from the measurement of $Cd_xZn_{1-x}S$ mixed crystals. It will be seen later that this predicted value is also erroneous. It has recently been suggested[7] that if a band corresponding to the long-wavelength ($\mathbf{k}\sim0$) transverse optic (TO) mode of the cubic ZnS(3*C*) does occur in the Raman spectrum, its intensity should be smaller than that of the band due to the $\mathbf{k}\sim0$ longitudinal optic (LO) phonon by at least a factor of 100. This observation is in disagreement with that of Couture-Mathieu and Mathieu,[8] who observed Raman bands

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