of optical studies. In cases where single-photon transitions between levels are forbidden for electric-dipole radiation, transitions can still be made by a doublephoton process. In order to study transitions to states that have large absorption coefficients by single-photon absorption, one normally requires thin samples, or one performs reflectivity experiments which can be sensitive to surface treatment. The fact that photons of energy less than the band gap can produce transitions to states of twice the energy of the incident photon can be used to study upper states by the use of thick samples since the double-photons transitions take place throughout the bulk of the material.

[Note added in proof. The observation of a twoquantum absorption spectrum employing a high-intensity laser and a low-intensity variable-frequency incoherent light source in an experiment of the type suggested in this paper has been performed by J. J. Hopfield, J. M. Warlock, and Kwangjai Park, Phys. Rev. Letters 11, 414 (1963) in KI.7

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Effect of an External Electric Field on the Velocity of Sound in Semiconductors and Semimetals

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A study is made of the effect of a dc electric field on the velocity of sound in semiconductors and semimetals. It is shown that the velocity of sound as a function of a dc field has either a maximum or minimum value at fields such that $V_d = S$. The particular cases studied are for acoustic waves propagating in an extrinsic semiconductor in a dc electric field and in a semimetal in crossed dc electric and magnetic fields.

I. INTRODUCTION

R ECENTLY, interest has been centered on the amplification of acoustic waves via their interaction with conduction electrons in semiconductors and semimetals.¹⁻⁵ The amplification occurs when there are dc electric fields present which give the conduction electrons a net drift velocity, V_d , in the direction of propagation of the acoustic wave which exceeds the sound velocity S. Since the presence of the dc electric field has such a strong effect on the electron sound-wave interaction, it is of interest to see whether dc electric fields will also alter measurably the velocity of sound.

The effect of the interaction of the conduction electrons and the sound wave on the velocity of sound has been calculated by several authors⁶⁻⁹ in the absence of dc electric fields. However, most of these calculations

are only valid in metals where all the atoms are ionized. This is because they all depend upon the calculation of dispersion relations for the self-consistent electromagnetic field which is generated by the passage of the sound wave. In nonpiezoelectric semiconductors and semimetals, on the other hand, only a very small number of atoms are ionized and the major interaction between the conduction electrons and the sound wave is via deformation potential forces. These forces arise from the deformation of the electronic energy bands resulting from the passage of the sound wave. In this paper we will consider the interaction between the carriers and the sound wave as arising solely from the deformation potential.

In Sec. II, we shall develop a formalism for treating the influence of the electron-phonon interaction on the propagation of sound waves, which is valid both for extrinsic semiconductors and semimetals. In Sec. III and IV we shall treat, respectively, the cases of an extrinsic semiconductor in the presence of a dc electric field and of a semimetal in crossed electric and magnetic fields. In Sec. V we will discuss the possibility of observing the effects calculated in the paper.

II. GENERAL THEORY

We consider a longitudinal acoustic wave propagating in the x direction of a medium and we define a strain S,

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a stress T, and a displacement u such that

$$S = \partial u / \partial x$$
 and $T = \rho \partial^2 u / \partial t^2$, (2.1)

where ρ is the mass density of our media. We assume that the sound wave interacts with the charged carriers via the deformation of the energy bands,

$$E_i = C_i S, \qquad (2.2)$$

where E_i is the interaction energy and where C_i is the deformation potential for the carriers of type *i*. We shall assume that we have two types of carriers, electrons and holes, and we treat them as free electron and hole gases. Then the equation for the stress, taking into account the electron sound-wave interaction,¹⁰ is

$$T = cS - nC_n - pC_p, \qquad (2.3)$$

where c is the ordinary elastic modulus and n and p are the densities of the electrons and holes. Using (2.1) together with (2.3) we obtain the following equation of the motion for the acoustic wave

$$\rho \frac{\partial^2 u}{\partial t^2} = c \frac{\partial^2 u}{\partial x^2} - C_n \frac{\partial n}{\partial x} - C_p \frac{\partial p}{\partial x}.$$
 (2.4)

For a sound wave of frequency ω and wave number q, $u \propto \exp[i(qx - \omega t)]$. When the effects of the sound wave can be treated as a perturbation on the motion of the electrons and holes, the electron and hole densities can be expressed as $n=n_0+n_1$, $p=p_0+p_1$, where n_0 and p_0 are the unperturbed densities and $n_1, p_1 \propto \exp[i(qx - \omega t)]$. Using the equations of continuity

$$-e\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{J}_n = 0, \quad e\frac{\partial p}{\partial t} + \nabla \cdot \mathbf{J}_p = 0, \qquad (2.5)$$

together with (2.4) we have

$$\omega^{2}\rho u = q^{2}cu - iq \left(C_{n}\mathbf{q} \cdot \frac{\mathbf{J}_{n}}{e\omega} - C_{p}\mathbf{q} \cdot \frac{\mathbf{J}_{p}}{e\omega} \right).$$
(2.6)

From previous work,¹¹⁻¹³ we can write for the constitutive equations of the electron and hole currents

$$\mathbf{J}_{n} = -\boldsymbol{\sigma}_{n} \cdot [\boldsymbol{\sigma}_{n} + \boldsymbol{\sigma}_{p} + \mathbf{B}]^{-1} \\
\cdot [\boldsymbol{\sigma}_{p} \cdot \mathbf{q}q(C_{n} + C_{p}) + \mathbf{B} \cdot \mathbf{q}qC_{n}](u/e), \quad (2.7)$$

$$\mathbf{J}_{p} = \boldsymbol{\sigma}_{p} \cdot [\boldsymbol{\sigma}_{n} + \boldsymbol{\sigma}_{p} + \mathbf{B}]^{-1}$$

$$\cdot [\sigma_n \cdot \mathbf{q}q(C_n + C_p) + \mathbf{B} \cdot \mathbf{q}qC_p](u/e)$$

where

$$\mathbf{B} = (i\omega/4\pi)(c/S)^2 \{ \mathbf{I} - [\mathbf{1} + (S/c)^2] \hat{q} \hat{q} \}, \quad (2.8)$$

and σ_n and σ_p are the electron and hole effective conductivity tensors in the presence of the sound wave.

Using (2.7) in (2.6) we obtain the following dispersion relation between the sound frequency and wave number:

$$\omega^2 = q^2 S_0^2 k \,, \tag{2.9}$$

where

$$k = 1 + (i/4e^{2}\omega\rho S_{0}^{2}) \{ (C_{n} + C_{p})^{2} \mathbf{q} \\ \cdot [\boldsymbol{\sigma}_{n} + \boldsymbol{\sigma}_{p} - (\boldsymbol{\sigma}_{n} - \boldsymbol{\sigma}_{p}) \cdot \boldsymbol{\Gamma} \cdot (\boldsymbol{\sigma}_{n} - \boldsymbol{\sigma}_{p})] \cdot \mathbf{q} \\ + (C_{n} - C_{p})^{2} \mathbf{q} \cdot \boldsymbol{\Gamma} \cdot \mathbf{B} \cdot (\boldsymbol{\sigma}_{n} + \boldsymbol{\sigma}_{p}) \cdot \mathbf{q} + (C_{n}^{2} - C_{p}^{2}) \mathbf{q} \quad (2.10) \\ \cdot [(\boldsymbol{\sigma}_{n} - \boldsymbol{\sigma}_{p}) \cdot \boldsymbol{\Gamma} \cdot \mathbf{B} + \boldsymbol{\Gamma} \cdot \mathbf{B} \cdot (\boldsymbol{\sigma}_{n} - \boldsymbol{\sigma}_{p})] \cdot \mathbf{q} \}, \\ \mathbf{\Gamma} = [\boldsymbol{\sigma}_{n} + \boldsymbol{\sigma}_{p} + \mathbf{B}]^{-1},$$

and $S_0 = (c/\rho)^{1/2}$ is the sound velocity in the absence of the electron sound-wave interaction. The velocity of sound and the attenuation or amplification coefficient can both be obtained from k

$$S = S_0 \operatorname{Re}\sqrt{k}; \quad \alpha = q \operatorname{Im}\sqrt{k}.$$
 (2.11)

We will in the next sections evaluate (2.10) and (2.11)for two specific cases.

III. EXTRINSIC SEMICONDUCTOR IN DC ELECTRIC FIELD

In the case where we have an extrinsic semiconductor, C_p and σ_p can be set equal to zero in (2.10). We can then write

$$k = 1 + q^2 \frac{C^2}{4\pi\rho e^2 S_0^2} \frac{\sigma_{xx}}{\sigma_{xx} - (i\omega/4\pi)}.$$
 (3.1)

Since the second term in (3.1) is usually much smaller than the first, the sound velocity and the attenuation coefficient can be obtained in terms of the component of the conductivity tensor in the direction of propagation

$$S = S_0 \left[1 + \frac{N_0 m}{2\rho} \left(\frac{V_F}{S_0} \right)^2 \left(\frac{q}{q_x} \right)^2 \times \left(\frac{C}{m V_F^2} \right)^2 \operatorname{Re} \frac{\sigma_{xx}}{\sigma_{xx} - (i\omega/4\pi)} \right], \quad (3.2a)$$

$$N_0 m \left(V_T \right)^2 \left(q \right)^2 \left(-C_T \right)^2 = \sigma_{xx}$$

$$\alpha = \frac{N_0 m}{2\rho} \left(\frac{V_F}{S_0}\right)^2 q \left(\frac{q}{q_d}\right)^2 \left(\frac{C}{m V_F^2}\right)^2 \operatorname{Im} \frac{\sigma_{xx}}{\sigma_{xx} - (i\omega/4\pi)}, \quad (3.2b)$$

where $q_d = V_F / \omega_p$ is the Debye wave number, ω_p $(4\pi N_0 e^2/m)^{1/2}$ is the plasma frequency, and V_F is the Fermi velocity of the electrons. Expression (3.2b) for the attenuation coefficient agrees with an expression derived by the author by another method for this coefficient.⁴ We shall only evaluate the expression for the change in the velocity of sound (3.2a) as (3.2b) would give the previously derived results for α . When ql < 1, the expression for σ_{xx} becomes⁴

$$\sigma_{xx} = \frac{\sigma_0}{\mu + (iqlV_F/3S_0)} \,. \tag{3.3}$$

Here σ_0 is the dc conductivity, *l* is the electron mean free

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path, and $\mu = 1 - (V_d/S_0)$, where V_d is the drift velocity in the dc electric field. Substituting (3.3) in (3.2a) we have

$$\frac{\Delta S}{S_0} = \frac{S - S_0}{S_0} = \frac{N_0 m}{2\rho} \left(\frac{C}{m S_0^2}\right)^2 \times \frac{(\omega_p \tau)^2 [1 + \frac{1}{3} (q/q_d)^2]}{\mu^2 + (\omega_p^2 \tau/\omega)^2 [1 + \frac{1}{3} (q/q_d)^2]^2}.$$
 (3.4)

In this case, the velocity of sound initially increases with increasing drift field, reaching its maximum value at $V_d = S_0$, and thereafter decreases with increasing drift velocity. The behavior of the velocity of sound as a function of drift velocity is shown in Fig. 1.

When ql > 1, σ_{xx} becomes⁴

$$\sigma_{xx} = -\frac{3\sigma_0}{ql} \frac{S_0}{V_F} \left[\frac{\mu \pi}{2} \frac{S_0}{V_F} - i \right].$$
(3.5)

Therefore, for ql > 1,

$$\frac{\Delta S}{S_0} = \frac{N_0 m}{2\rho} (\omega/\omega_p)^2 (C/mS_0^2)^2 \left[1 + \frac{1}{3} \left(\frac{q}{q_d}\right)^2 + \left(\frac{\pi}{2} \frac{S_0}{V_F}\right)^2 \right] / \left[1 + \frac{1}{3} \left(\frac{q}{q_d}\right)^2 \right]^2. \quad (3.6)$$

In this case, the velocity of sound has its minimum value when $V_d = S_0$. The behavior of the velocity of sound with drift velocity for this case is shown in Fig. 2.

IV. SEMIMETAL IN CROSSED ELECTRIC AND MAGNETIC FIELDS

In the case of a semimetal in crossed electric and magnetic fields, we must use the general expression (2.10) for k. However, the following assumption can be made



FIG. 1. The normalized change in sound velocity, $2(\Delta S/S_0) \times (\rho/N_0 m) (mS_0^2/C)^2/(\omega_p \tau)^2 [1+\frac{1}{3}(q/q_d)^2]$, is shown as a function of V_d/S_0 in an extrinsic semiconductor when ql < 1. We have used the values $\omega_p = 10^{12} \sec^{-1}$, $\omega = 10^{10} \sec^{-1}$, and $\tau = 10^{-11} \sec$.



FIG. 2. The normalized change in the velocity of sound, $2(\Delta S/S_0) \times (\rho/N_0 m) (\omega_p/\omega)^2 (mS_q^2/C)^2$, is plotted versus the ratio of drift velocity to sound velocity, V_d/S_0 , in an extrinsic semiconductor when ql > 1 and $q < q_d$.

for the sake of simplifying our calculations. The assumption will be to assume that the electrons and holes have equal masses and relaxation times. This assumption will affect the final results quantitatively but not qualitatively. For all the attainable sound frequencies, the term containing the sum of the deformation potentials will dominate the remaining terms. Then we can write

$$k = 1 + \frac{iq^2}{2\rho e^2 \omega S_0^2} (C_n + C_p)^2 \sigma_{xx}.$$
 (4.1)

Here again, the second term is usually smaller than the first and one obtains, as in (3.2), both the sound velocity and the attenuation coefficient in terms of σ_{xx} :

$$S = S_0 \left[1 - \frac{\pi N_0 m}{\rho \omega} \left(\frac{V_F}{S_0} \right)^2 \left(\frac{q}{q_d} \right)^2 \left(\frac{C_n + C_p}{m V_F^2} \right)^2 \operatorname{Im} \sigma_{xx} \right],$$
(4.2a)

$$\alpha = \frac{\pi N_0 mq}{\omega \rho} \left(\frac{V_F}{S_0} \right)^2 \left(\frac{q}{q_d} \right)^2 \left(\frac{C_n + C_p}{m V_F^2} \right)^2 \operatorname{Re}\sigma_{xx}.$$
(4.2b)

The expression (4.2b) for the attenuation coefficient agrees with the expressions derived by other methods for this quantity.^{4,5,12} Therefore, we will explicitly evaluate the expression for the change in the velocity of sound for several cases of interest.

When the conditions $\omega_c \gg \omega$ and $\omega_c \tau \gg 1$ are satisfied, where ω_c is the cyclotron frequency of the carriers, the following expression for σ_{xx} is obtained⁴:

$$\sigma_{xx} = \frac{3\sigma_0}{(ql)^2} \frac{(1 - i\omega\mu\tau)(1 - g_0(X))}{\mu + (i/\omega\tau)(1 - g_0(X))}.$$
(4.3)

In (4.3), $X = qV_F/\omega_c$, $\mu = 1 - (V_H/S_0)$, where V_H is the electron drift velocity in the crossed electric and magnetic field and $g_0(X)$ is an oscillatory function of X de-



FIG. 3. The normalized change in sound velocity, $(\Delta S/S_0) \times (\rho/N_0 m X^2) (S_0/V_F)^2 (m V_F^2/C)^2$, is shown as a function of V_H/S_0 in a semimetal in the high-field limit. We have used the values X=0.1 and $\omega_c \tau = 10^2$.

fined in Ref. 11. Using (4.3) in (4.2a) we find

$$\frac{\Delta S}{S_0} = \frac{3}{4} \frac{N_0 m}{\rho} \left(\frac{V_F}{S_0} \right)^2 \left(\frac{C_n + C_p}{m V_F^2} \right)^2 (1 - g_0) \\ \times \left[\frac{\mu^2 + \left[(1 - g_0) / (\omega \tau)^2 \right]}{\mu^2 + \left[(1 - g_0) / \omega \tau \right]^2} \right]. \quad (4.4)$$

Here, too, the velocity of sound has a maximum value at $V_H = S_0$. The behavior of (4.4) with drift velocity is shown in Figure 3 in the high-field limit. In this limit $X \ll 1$, $g_0(X) = 1 - \frac{1}{3}X^2$, and (4.4) has the form

$$\frac{\Delta S}{S_0} = \frac{1}{4} \frac{N_0 m}{\rho} \left(\frac{V_F}{S_0} \right)^2 \left(\frac{C_n + C_p}{m V_F^2} \right)^2 (ql)^2 \\ \times \left[\frac{\mu^2 (\omega_c \tau)^2 + \frac{1}{3} (V_F/S_0)^2}{\mu^2 (\omega_c \tau)^4 + \frac{1}{9} (ql)^2 (V_F/S_0)^2} \right]. \quad (4.5)$$

In the region where cyclotron resonance appears, σ_{xx} has the form⁴

$$\sigma_{xx} = \frac{-3i\sigma_0}{ql} \frac{S_0}{V_F} \left[1 + \frac{i\pi\omega\mu\tau}{2ql} \coth\frac{(1-i\omega\mu\tau)\pi}{\omega_c\tau} \right]. \quad (4.6)$$

The change of the velocity of sound in this region is

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$$\frac{\Delta S}{S_0} = \frac{3N_0 m}{4\rho} \left(\frac{V_F}{S_0}\right)^2 \left(\frac{C_n + C_p}{m V_F^2}\right)^2 \times \left[1 - \frac{\pi}{2} \frac{S_0}{V_F} \operatorname{Im coth} \frac{(1 - i\omega\mu\tau)}{\omega_c \tau} \pi\right]. \quad (4.7)$$

The velocity of sound has maxima and minima at values of the drift velocity which are solutions of the complicated transcendental equation

$$\frac{d}{d\mu} \left[\frac{\mu \tan(\omega\mu\pi/\omega_c)}{\tanh^2(\pi/\omega_c\tau) + \tan^2(\omega\mu\pi/\omega_c)} \right] = 0.$$
(4.8)

The velocity of sound as a function of V_H for this case is shown in Fig. 4. The velocity of sound has a maxima when $V_H = S_0$.

In the region where quantum effects occur, σ_{xx} becomes⁴

$$\sigma_{xx} = \sigma_0 \frac{(1 - i\omega\mu\tau)(1 + F)}{\mu + (i/3)(X^2/\omega\tau)(1 + F)},$$
(4.9)

where

$$F = 3\sqrt{2}\pi^2 \frac{kT}{\hbar\omega_c} \left(\frac{\hbar\omega_c}{E_F}\right)^{1/2} \sum_{r=0}^{\infty} \frac{\cos(2\pi r E_F/\hbar\omega_c - \frac{1}{4}\pi)}{\sinh(2\pi^2 r k T/\hbar\omega_c)}$$

In (4.9), E_F is the Fermi energy, T is the temperature, and k is Boltzmann's constant. Thus in the region where the de Haas-van Alphen oscillations occur in other transport phenomena, they are also found in the velocity of sound.

$$\frac{\Delta S}{S_0} = \frac{N_0 m}{4\rho} \left(\frac{C_n + C_p}{m V_F^2} \right)^2 \left(\frac{V_F}{S_0} \right)^2 \\ \times \left[\frac{(\omega_c \tau)^2 \mu^2 + \frac{1}{3} (V_F / S_0)^2 (1+F)}{\mu^2 (\omega_c \tau)^4 + \frac{1}{9} (V_F / S_0)^2 (ql)^2 (1+F)^2} \right]. \quad (4.10)$$

The behavior of the velocity of sound as a function of the drift velocity is the same as that shown in Fig. 3.

The above results are all for the case when the magnetic field is transverse to the direction of propagation of the sound wave. When the magnetic field and the



FIG. 4. The normalized change in sound velocity, $(\Delta S/S_0) \times (\rho/3N_0m)(S_0/V_F)^2(mV_F^2/C)^2$, is plotted as a function of V_H/S_0 in a semimetal under conditions of cyclotron resonance. We have taken $\omega/\omega_c = \frac{3}{4}$ and $\omega_c \tau = 10$.

direction of propagation of the sound wave are no longer transverse, the above results can be generalized by using the appropriate expression for the σ_{xx} component of the conductivity tensor.

V. DISCUSSION

Our calculations have shown that there is a dependence of the velocity of sound in a semiconductor or semimetal on an applied dc electric field. We have found that the velocity of sound has either a maximum or minimum value as a function of electric field when $V_d = S_0$. This results because the maximum interaction between the conduction electrons and the sound wave occurs when the electrons have a net drift velocity in the direction of propagation which is equal to the velocity of sound. We can use the zero-field value of the velocity of sound in all our expressions, since the corrections resulting from the field are small compared to S_0 .

The question now arises as to the conditions under which the change in the velocity of sound is measurable. It is possible, at present, to measure velocity changes by one part in 10⁵ using the conventional pulse technique.¹⁴ It is estimated, that when the present techniques are improved, a measurement of velocity changes of one part in 10^7 would be possible. Since the maximum effect of the dc electric field on the velocity of sound occurs when $V_d = S_0$, and the attenuation due to the sound-wave conduction electron interaction vanishes at this point, there would be no complications arising from a large attenuation or amplification of the wave.

The change of velocity to be measured is that between the value at zero dc field and at the field where $V_d = S_0$. In an extrinsic semiconductor with $N_0 = 10^{14}$ electrons/cm³, $m = 10^{-28}$ g and C = 10 eV the maximum change of $\Delta S/S_0 \sim 10^{-5}$ occurs for ql < 1, while for ql > 1, the maximum change would only be $\Delta S/S_0 \sim 10^{-9}$. For ql < 1, the maximum change should be measurable and occur for ω between 10⁸ and 10¹⁰ cycles/sec. The change when ql > 1 would not be measurable under present conditions. For a semimetal, with a density of $N_0 = 5 \times 10^{17}$ electrons/cm³ and a deformation potential of 10 eV, the change of velocity in the crossed fields would be $\Delta S/S_0 \sim 10^{-1}$ and should easily be measurable.

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Superconductivity in Many-Valley Semiconductors and in Semimetals^{*}

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It is shown that the attractive electron-electron interaction arising from the exchange of intravalley and intervalley phonons can be larger than the repulsive Coulomb interaction in many-valley semiconductors and semimetals and can cause these materials to exhibit superconducting properties. The importance of observing a superconducting transition in these materials and the properties required of a semiconductor or semimetal to maximize its superconducting transition temperature are discussed.

I. INTRODUCTION

I N early work on materials below 1°K, nondegenerate semiconductors were tested along with metals for superconductivity; however, none were found to exhibit a superconducting transition. In particular, Ge and Si were examined, and these semiconductors were found to remain in a normal state down to 0.05°K¹ and 0.073°K,² respectively.

When one considers the small number of free carriers available in a nondegenerate semiconductor below 1°K, these results are not surprising and are consistent with the Bardeen-Cooper-Schrieffer (BCS)³ theory of superconductivity.

However, even after the advent of the BCS theory, the question of the existence of a superconducting state in a degenerate semiconductor or a semimetal remained unanswered,⁴ and, despite the paucity of published work on this problem, it has been frequently explored both theoretically and experimentally.

In previous theoretical investigations, only intravalley processes in a single-valley conduction band and a single-valley valence band had been considered, and

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