Collective Phonon-Electron Waves and Oscillations in Piezoelectric Materials

E. W. PROHOFSKY
Sperry Rand Research Center, Sudbury, Massachusetts
(Received 24 July 1964)

The behavior of collective phonon waves interacting with a drifting electron distribution under conditions of acoustic gain in piezoelectric materials is analyzed and discussed. The electrons are bunched by the phonons, and the resulting electrostatic fields become an important element in the collective-wave behavior. This results in a tendency to set up an electrostatic oscillation involving phonons as well as electrons. The oscillation frequency is the plasma frequency for electrons with mass heavily dressed by the phonons. In CdS, this frequency is about 10^5 sec^{-1}. The collective wave exhibits a great deal of dispersion and is greatly amplified at frequencies near the oscillation frequency. It is believed that the spontaneous oscillations observed in piezoelectric materials at large drift velocities are the collective waves described in this analysis. The oscillations involve wavelengths which are simultaneously those of the electrostatic oscillation frequency and multiples of the length of the crystal involved.

I. INTRODUCTION

THIS paper analyzes the collective behavior of electrons and a strongly coupled band of phonons (hereinafter referred to as the active band) under conditions of acoustic gain. It is found that a new collective phenomenon exists which can best be characterized as an electrostatic oscillation in which the electrons and the active-band phonons participate. It is believed that those spontaneous current oscillations observed under conditions of acoustic gain which are not associated with simple ultrasonic ringing are related to this phenomenon.[1] The predictions of this theory agree qualitatively with the observed oscillations as a function of electron density in CdS. Spontaneous oscillations, which have been reported in other materials,[2] may also be related to the collective phenomenon described here.

In a previous theoretical development of collective-wave propagation[3] (hereinafter referred to as paper I), it was shown that a restricted band of phonons could be amplified by drifting electrons and support collective phonon waves similar to second-sound propagation in He II. However, in that analysis, the accumulation of charge which is expected to be associated with the collective wave was not included. This restricted the validity of the analysis to short wavelengths where charge accumulation is least important.

The effects of this accumulation become important, and even dominant, at long wavelengths, giving rise to the oscillation behavior mentioned above. In the case of the spontaneous oscillations, wavelengths are the order of the size of the crystals.

The behavior of these collective waves can be likened to the oscillatory motion of a mass supported by two springs in parallel whose spring constants can be altered. The frequency of oscillation will be determined by the stiffest spring. In the analogy to the collective wave, one spring would be that of the phonon-density gradient. This spring constant increases quadratically with collective wave vector. The other spring is that of the electrostatic forces due to electron density fluctuations. The "spring constant" of this force increases for smaller wave vectors, as the electron bunching is greatest for long wavelengths. In the short-wavelength limit, the collective wave will be dominated by the phonon-gradient "spring," and the wave will be similar to second sound, somewhat affected by, or dressed by, electrons. In the long-wavelength limit, the wave will be dominated by electron forces somewhat affected by, or dressed by, phonon-density fluctuations. In the intermediate-wavelength region the two "springs" are roughly equal, and the collective wave has the nature of both an electrostatic oscillation and a phonon-density wave. The spontaneous oscillations are associated mainly with the electrostatic wave aspects of the collective waves.

In Sec. II, a phenomenological description of the collective wave is given which stresses the difference between the interaction of the collective wave with electrons and the interaction of a coherent ultrasonic wave with electrons. The coupling of these collective waves with the experimental configuration used in observing spontaneous oscillations is discussed.

In Sec. III, first-order moment equations, representing the phonon-crystal momentum, phonon energy, electron momentum, electron density and Poisson's equation, are simultaneously solved, and the resulting dispersion relation for the collective behavior of these elements is analyzed. The use of these moment equations is similar to the use of hydrodynamic equations in that the variables are equivalent to densities and drift velocities. The resulting solutions can be separated into three distinct regions: (1) the short-wavelength region which is the simple collective-phonon propagation analyzed in paper I, (2) the intermediate-wavelength region in which spontaneous oscillations are likely to occur, and (3) the long-wavelength region in which the collective wave degenerates into an electron-density fluctuation traveling at the electron-drift velocity. A cutoff for the collective waves occurs at some frequency

[1] H. Kroger, E. W. Prohofsky, and H. R. Carleton, Phys. Rev. Letters **12**, 555 (1964).
[2] J. B. Gunn, Solid State Commun. **1**, 88 (1963); J. B. Gunn, IBM J. Res. Develop. **8**, 141 (1964).
[3] E. W. Prohofsky, Phys. Rev. **134**, A1302 (1964); R. W. Damon, H. Kroger, and E. W. Prohofsky, Proc. IEEE **52**, 912 (1964).

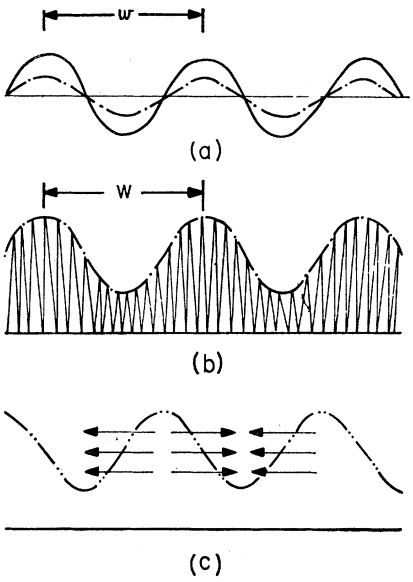

FIG. 1. (a) The large-amplitude sine wave (solid line) with wavelength w represents the electric potential associated with a coherent sound wave in piezoelectric material. The accumulation of electrons in regions of positive potential reduces the potential. The sound wave with accumulated charge is represented by the broken-line sine wave. The largest amount of charge accumulation which can occur would completely counterbalance the piezoelectric potential, in which case no further electron attraction occurs. (b) The broken sine wave in (b) represents the density of phonons. The phonon distribution has a density fluctuation which corresponds to a collective wave with wavelength W. There is no coherent electric potential associated with this wave. The local electric potentials are associated with the short-wavelength phonons $w \ll W$ and are represented by the jagged lines contained within the density fluctuation. The individual electrons interact with the potentials of individual phonons. The total effect of the phonon-density fluctuation with period W is to give rise to a resistance fluctuation felt by the entire electron distribution with period W. (c) The resistance fluctuation causes the accumulation of space charge diagrammed in (c). Since no net piezoelectric potentials exist over distances W the only contribution to coherent potentials comes from the accumulated charge. The phase relationship between charge density and electric potential in this situation is opposite to that which exists in (a). The electric fields due to charge accumulation represented by arrows in (c) are such as to increase phonon emission in the regions of highest phonon density.

below the intermediate region. No wavelike solutions exist for all lower frequencies.

In Sec. IV, the behavior of the spontaneous oscillations predicted by this analysis is described.

II. PHENOMENOLOGICAL DESCRIPTION

A "phonon fluid" may, in principle, propagate a density fluctuation which is similar to a sound wave in ordinary fluids. The phonon-density fluctuations set up temperature gradients which play the same role as pressure gradients which would be set up by the density fluctuations in ordinary fluids. For these waves to exist, however, the loss or gain of momentum per cycle must be a small part of the total momentum associated with the wave.

Under conditions of acoustic gain, the large electron-drift velocity can supply momentum to a restricted group of phonons which can overcome the usual losses, making collective-wave propagation possible.

In paper I, it was shown that one would expect this to be the case in CdS, where the phonon fluid was comprised of a band of piezoelectric phonons with frequency centered about $\hbar\omega/v_s^2 \approx m_e^*$, where v_s is the velocity of sound and m_e^* the electron effective mass. The existence of phonon-phonon collision losses[4] would cause the higher frequency phonons to be damped more heavily than those at lower frequencies. Because of this, the phonons participating in collective phenomena may be of lower frequencies than indicated by the maximum in the analysis of the gain. These phonons can be considered a somewhat isolated fluid as they interact strongly with each other via higher order electron-phonon interactions and are fairly well isolated from other phonon modes of the crystal by a relaxation bottleneck.

The interaction between electrons and such a collective phonon wave is considerably different from the interaction between electrons and a single coherent sound wave. For example, a coherent piezoelectric sound wave appears to the electrons as a sinusoidally varying electric potential. This is diagrammed in Fig. 1(a). The electrons tend to accumulate in the regions of positive potential.[5] This accumulation of negative charge, however, decreases the potential, reducing the tendency to accumulate more charge. This process cannot make the regions of high-electron density regions of negative potential, since the reason for further charge accumulation vanishes at zero potential.

In the case of a collective phonon wave, there is no coherent piezoelectric potential associated with the collective wavelength. This case is diagrammed in Fig. 1(b). The coherent potentials are associated with the individual phonons making up the collective wave, and these phonon wavelengths w are considered small compared to the collective wavelength W. The phonons making up the collective wave are randomly distributed with random phase within the collective wave; only the density of the phonons varies coherently. The regions of large phonon density appear as regions of large resistance in electron flow. Drifting electrons will tend to bunch against the high-resistance regions as diagrammed in Fig. 1(c). Accumulations of space charge over distances of the order of collective wavelengths have negative potential, as there is no long-range piezoelectric potential to overcome.

The electrostatic fields associated with the space charge are represented by arrows in Fig. 1(c). These fields cause the larger voltage drop which occurs across regions of large resistance. The fields are oriented so as to accelerate the electrons in the regions of large phonon density and deaccelerate the electrons in the regions of

[4] T. O. Woodruff and H. Ehrenreich, Phys. Rev. **123**, 1553 (1961).

[5] D. L. White, J. Appl. Phys. **33**, 2547 (1962).

low density. In addition, the large phonon density stimulates a greater number of phonon emissions in these regions. That is, large resistance implies greater electron-phonon interactions. This selectivity in the rate of emission further increases the phonon density in dense regions which in turn increases the space-charge accumulation, etc. In this sense, these phonon-electron density distributions form a normal mode. It is different from most normal modes, as it requires external electric fields to give rise to the necessary electron-drift velocities.

Returning now to the situation considered in paper I, any propagating collective-phonon wave in the presence of rapidly drifting electrons will cause a bunching of electrons. In the limit of small electron bunching, the repelling potentials associated with the bunching cause an increase in the frequency. This frequency rise becomes more important at lower frequencies and it brings about an increase in the phase velocity of the collective wave.

In the intermediate-wavelength region the collective wave phase velocity becomes comparable to the electron-drift velocity, and the bunching of electrons within the wave greatly increases. In this region, the effect of charge bunching and the electrostatic field become of comparable importance to the phonon temperature fluctuations, and the character of the collective wave is considerably modified. At these intermediate wavelengths, the negative potential in the region of large electron density is similar to the situation which occurs in a plasma oscillation, and the electrostatic field would give rise to oscillatory motion of the charged particles. However, the electrons are not free to respond to this field as they are strongly coupled to the phonon density distribution. The only motions available to the electrons are those which displace the phonon density as well. The mass associated with this behavior is the combined mass of the phonons and electrons, which is essentially the phonon mass. The wave in this region is amplified since its phase velocity is comparable to, or less than, the electron-drift velocity; and energy transfer to the collective wave can occur.

In this intermediate region, where the frequency of the wave is increased by the electrostatic or "plasmalike effects," the dispersion curve $\Omega(Q)$ can be flat or even have negative slope. At still lower frequencies, the dispersion curve is modified, as the unmodified electrostatic wave would have a phase velocity greater than the electron-drift velocity. This would cause the electron and phonon-density fluctuation to become decoupled. The modified dispersion relation in this region degenerates into an electron density fluctuation traveling at the electron-drift velocity and locally causing distortions in the phonon distribution. This situation is highly unstable, as the collective wave is in resonance with the electron-drift velocity, causing the growth rate of such a wave to exceed the frequency. The wavelike solutions in this limit have no meaning and do not represent modes of the system.

The spontaneous oscillations occur when a feedback mechanism exists which can maintain oscillations. The feedback mechanism can exist when the wavelength of the collective wave becomes comparable to the length of the crystals. If this wavelength is in the intermediate region, large electrostatic fields extending over the length of the crystal will be present. The application of a fixed voltage across the crystal, from a low-impedance source, will select those electrostatic waves which give rise to time-independent voltage drops across the crystal. The external circuitry applies a boundary condition which in linearized form becomes

$$\int E_1(x,t)dx=0, \tag{2.1}$$

where $E_1(x,t)$ is the ac part of the electric field of the collective wave.

As pointed out previously,[1] in a macroscopic view, the effect of space charge and its associated eleotrostatic field would be described in terms of a greater voltage drop occurring over the regions of large phonon density. With a fixed voltage across the crystal there would be a smaller voltage drop across regions of low phonon density. This difference in voltage across various regions gives rise to differences in the phonon emission in the different regions, and this, coupled with a flow of the phonon-density fluctuations down the crystal, would give rise to oscillations.

III. SOLUTION OF THE MOMENT EQUATIONS

The model system being studied consists of a free-electron distribution which is strongly interacting with a particular group of phonon states called the active phonon band. The rate of interaction of the electrons and the active-band phonons with other phonon states (and all other degrees of freedom of the crystal) is considered to be much slower than the rate of interactions between the electrons and the active phonon band. It is assumed that the loss of crystal momentum and energy, by the system to the other degrees of freedom, can be adequately described by relaxation-time approximations. The transport properties of the active phonon band must satisfy the energy and crystal-momentum conservation equations

$$(\partial/\partial t)\langle\mathcal{E}\rangle+(\partial/\partial x_j)\langle v_j\mathcal{E}\rangle=\Delta\mathcal{E}_{\mathrm{col}}, \tag{3.1}$$

$$(\partial/\partial t)\langle P_i\rangle+(\partial/\partial x_j)\langle P_i v_j\rangle=\Delta P_{i\,\mathrm{col}}, \tag{3.2}$$

where the brackets $\langle\ \rangle$ imply a summation has been taken over all states making up the active phonon band, $\mathcal{E}$ is phonon energy, v_j is the jth component of phonon velocity, and P_i is the ith component of the phonon-crystal momentum. These equations have been discussed in Paper I.

Similarly, the transport properties of the electron distribution satisfy the equations of momentum and particle conservation

$$\frac{\partial}{\partial t}\langle p_i\rangle+\frac{\partial}{\partial x_j}\langle v_j p_i\rangle-E_j e\left\langle\frac{\partial f}{\partial p_j}p_i\right\rangle=\Delta p_{i\,\mathrm{col}}, \quad (3.3)$$

$$(\partial/\partial t)\langle n\rangle+(\partial/\partial x_j)\langle v_j n\rangle=0. \quad (3.4)$$

In this case, the brackets imply a summation over all electron states, p_i is the ith component of electron momentum, v_j is the jth component of electron velocity, n the electron density, e the electronic charge, and E_j is the jth component of the electric fields.

When local fluctuations in the electron density occur, electrostatic fields are set up. The fields, due to these space-charge effects are described by Poisson's equation

$$(\partial/\partial x_j)E_j=(4\pi en/\epsilon), \quad (3.5)$$

where ϵ is the dielectric constant. When the electrons and phonons are strongly interacting, and when distortions in the distribution of either affect the interaction rate, Eqs. (3.1)–(3.5) should be solved simultaneously. Equation (3.3) can be simplified by restricting the solutions to frequencies much smaller than the frequency of electron relaxation. The frequencies here are the collective-modulation frequencies Ω, not the frequency of individual phonons ω which may be a part of the system. In these low modulation-frequency regions, the transport behavior of the electrons is determined by the electric fields acting on them and the resistance they encounter. Equation (3.3) becomes

$$eE[(\partial f/\partial k)p]=\Delta(p)_{\mathrm{col}}. \quad (3.6)$$

In this equation, the electron inertial terms have been ignored. This is equivalent to excluding all electron-plasma effects.

As in Paper I, it is assumed that the disturbances in both the electron and phonon distributions can be described in terms of departures from equilibrium distributions. This requires a rate of normal collisions within the system which is fast compared to the frequencies of interest Ω. It is assumed that to first order these disturbances can be described by macroscopic parameters which correspond to net-drift velocities and quasiparticle densities. The simplest distribution functions which incorporate these parameters are

$$N(\omega,q)=[\exp(\hbar\omega-\hbar\lambda q/K(T_0+T_1))-1]^{-1} \quad (3.7)$$

$$f(\mathcal{E},k)=\left[\exp\left(\frac{\mathcal{E}-\hbar k(v_d+v_1)-\mathcal{E}_F(n_0+n_1)}{kT_0}\right)+1\right]^{-1}, \quad (3.8)$$

where T_0 is the ambient temperature, T_1 the local variations in phonon temperature, n_0 the ambient electron density, n_1 the local variations in electron density, v_d the electron-drift velocity, and v_1 the local variations in electron-drift velocity. Making use of a linearized expansion of Eqs. (3.7) and (3.8) to evaluate the moments on the left-hand side of Eqs. (3.1), (3.2), (3.4), and (3.6), they become

$$(\partial/\partial t)M\lambda_1+(\partial/\partial x)\gamma^2 CT_1=(\Delta P)_{\mathrm{col}}, \quad (3.9)$$

$$(\partial/\partial t)CT_1+(\partial/\partial x)D\lambda_1=v_s(\Delta P)_{\mathrm{col}}, \quad (3.10)$$

$$(-nm\mu/\tau_e)(E_0+E_1)=(\Delta p)_{\mathrm{col}}, \quad (3.11)$$

$$\frac{\partial}{\partial t}n_1+v_d\frac{\partial}{\partial x}n_1+n_0\frac{\partial}{\partial x}v_1=0, \quad (3.12)$$

where $\gamma\approx 1/\sqrt{3}$ because of the angular spread of the various phonons contributing to the transport of the collective wave

$$M=\frac{P}{\lambda}=\frac{1}{8\pi^3}\int_{q<q_{\max}}\hbar q\cos\theta\frac{\cos\theta\hbar q}{kT_0}\times N_0(q)[N_0(q)+1]d^3q, \quad (3.13)$$

$$D=\frac{1}{8\pi^3}\int_{q<q_{\max}}(\hbar v_s q)(v_s\cos\theta)\frac{\hbar q\cos\theta}{kT_0}\times N_0(q)[N_0(q)+1]d^3q. \quad (3.14)$$

$D/M\approx v_s^2$, and C is the phonon specific heat summed over all states; $q<q_{\max}$, where $q_{\max}$ is the upper limit of the active-phonon band. Extending the lower limit of these integrals to $q=0$, even though long-wavelength phonons play little or no role, does not greatly affect these parameters. M is, in a sense, the inertial mass per unit volume of the active phonon band.

The expression $\langle(\partial f/\partial k)p\rangle$ has been replaced by $nm\mu/\tau_e$, where μ is the normal mobility assumed constant, i.e., evaluated at drift velocities less than the sound velocity where no saturation effects occur, and where a simple relaxation time τ_e is sufficient to describe the resistive processes.

When the electron-drift velocity is greater than the velocity of sound, an electron-population inversion exists with respect to phonon emission. In such a case, the right-hand side of Eqs. (3.9)–(3.11) can be written in linearized form as discussed in Paper I as

$$(\Delta P)_{\mathrm{col}}=Xv_1+Y\lambda_1+Zn_1-(M\lambda_1/\tau_P), \quad (3.15)$$

$$(\Delta E)_{\mathrm{col}}=v_s(\Delta P)_{\mathrm{col}}, \quad (3.16)$$

$$(\Delta p)_{\mathrm{col}}=-Xv_1-Y\lambda_1-Zn_1-[(n_0+n_1)m(v_d+v_1)/\tau_e], \quad (3.17)$$

where X is the linearized coefficient of the increase in local phonon emission due to local increases in the electron-drift velocity, Y is the coefficient associated with the local increase in stimulation occurring with increases in λ_1, and Z is the local increase in emission due to larger local electron densities. Because the interac-

tion is basically due to velocity-induced population inversions, we expect Z/X or Z/Y to be small except at largest drift velocities.

It should be pointed out that the phonon emission term developed in Paper I applies only when $q\ell>1$, where q is the wave vector of the phonon in the collective wave, and ℓ is the electron mean free path. For those phonons participating in the collective wave which do not satisfy this condition, one should use an interaction term based on a classical analysis such as that of White.[5] At present, it is not completely clear which phonon frequencies are most important in the collective wave, as the rate of phonon-phonon collision losses is not known. It has been shown that the mixing rate for classical phonons ($q\ell<1$) under gain conditions is quite fast,[6] and these phonons could take part in collective wave propagation. In any case, one can define an electron-phonon interaction term which can be linearized in some region as described above, and the equations then become

$$\frac{\partial}{\partial t}M\lambda+\frac{\partial}{\partial x}\gamma^2CT_1=(Y-M/\tau_p)\lambda_1+Xv_1+Zn_1, \tag{3.18}$$

$$\frac{\partial}{\partial t}CT_1+\frac{\partial}{\partial x}D\lambda_1=v_s(Y-M/\tau_p)\lambda_1+v_sXv_1+v_sZn_1, \tag{3.19}$$

$$\frac{m\mu}{\tau_e}E_0n_1+\frac{n_0m\mu}{\tau_e}E_1=-\left(X+\frac{n_0m}{\tau_e}\right)v_1-Y\lambda_1-Zn_1+\frac{mv_d}{\tau_e}n_1, \tag{3.20}$$

$$\frac{\partial}{\partial t}n_1+\frac{\partial}{\partial x}v_dn_1+\frac{\partial}{\partial x}n_0v_1=0, \tag{3.21}$$

$$\frac{\partial}{\partial x}E_1=\frac{4\pi e}{\epsilon}n_1. \tag{3.22}$$

In infinite and isotropic material, one would look for plane-wave solutions to exist where

$$T_1,\lambda_1,v_1,n_1,E_1\propto e^{i(\Omega t-Qx)}. \tag{3.23}$$

Substituting Eq. (3.23) into Eqs. (3.18)–(3.22), one can solve for the dispersion relation of the combined system, which is

$$\alpha_1\alpha_2\alpha_3+\eta\alpha_1\alpha_2\alpha_4+\frac{n_0Z}{X}Q\alpha_1\alpha_2+\frac{\Delta}{X}\Omega_0^2\alpha_5=i\left[\eta\frac{\Delta}{M}\alpha_4\alpha_5-\frac{\Omega_0^2}{X}M\alpha_1\alpha_2-\tau_p^{-1}\alpha^3\alpha^5-\frac{n_0Z}{X}\tau_p^{-1}Q\alpha_5\right], \tag{3.24}$$

where the undisturbed roots of the equations are

$$\alpha_1=(\Omega+\gamma v_sQ), \tag{3.25}$$

$$\alpha_2=(\Omega-\gamma v_sQ), \tag{3.26}$$

$$\alpha_3=(\Omega-v_dQ), \tag{3.27}$$

$$\alpha_4=(\Omega-\mu E_0Q), \tag{3.28}$$

$$\alpha_5=(\Omega+\gamma^2v_sQ), \tag{3.29}$$

and

$$\Omega_0^2=\frac{n_0m}{M}\omega_p^2=\frac{4\pi e^2n_0}{\epsilon M/n_0}, \tag{3.30}$$

$$\Delta=Y-M/\tau_p, \tag{3.31}$$

$$\eta=\frac{n_0m/\tau_e}{X}. \tag{3.32}$$

Ω_0 is a plasma frequency for charged particles with the charge of an electron and a mass M/n_0, which is the phonon mass per electron.

The quantity Δ is related to the net stimulated rate of growth of the phonon crystal momentum. As pointed out earlier, Y is that part of the momentum transfer driven by the ac phonon amplitude. The term M/τ_p is the momentum loss driven by the same ac phonon amplitude. The term X is the rate of crystal momentum transfer driven by displacements of the electron distribution, as distinguished from Y, which is driven by the phonon displacement. This momentum-transfer term is not selective, as momentum is pumped to both the ac phonon wave as well as the dc thermal background. The ratio of Δ/X, then, is a measure of both the viscosity and selectivity of the electron-phonon collective-wave interaction. The larger this ratio is, the better the coupling of the ac component of the phonon wave to the electrons.

The factor n_0m/τ_e is the rate of usual resistive losses of electrons in the absence of inverted populations and strong coupling to phonons. The factor X is also that part of the electron resistive losses specifically related to the inverted population. It is the term responsible for the saturation of currents observed when $v_d>v_s$. The factor η is the ratio of these two electron loss mechanisms. The cases of interest are assumed to have strong interactions, and we assume for simplicity that $\eta\ll1$. However, $\eta\mu E_0$ is comparable to v_d. In the absence of a very strong electron-active phonon-band interaction, $v_d=\mu E_0$. When the current is saturated, one expects v_d to be reduced from μE_0 by the ratio η; therefore,

$$\eta\mu E_0\approx v_d. \tag{3.33}$$

A physically revealing approximate solution of Eq. (3.21) can be made for very short wavelengths. From the previous analysis in Paper I, one expects that at short wavelengths

$$\Omega\approx\gamma v_sQ, \tag{3.34}$$

[6] H. Kroger, Appl. Phys. Letters 4, 190 (1964).

where $\gamma v_s < v_s \lesssim v_d$, and the root α_3 is far from resonance. In this case, one can divide Eq. (3.24) by α_3 and use Eq. (3.34) to eliminate the ratios of Ω/Q which occur in the denoninator.

Substituting from Eqs. (3.25)–(3.29), this becomes

$$\Omega^2=\gamma^2 v_s^2 Q^2+\Omega_0^2\frac{\gamma(1+\gamma)}{[(v_d/v_s)-\gamma][2(v_d/v_s)-\gamma]}\frac{\Delta}{X}$$
$$+i\frac{(\Omega+\gamma^2 v_s Q)}{[2(v_d/v_s)-\gamma]}\left[\left(\frac{Y}{M}-\frac{1}{\tau_p}\right)\eta\frac{\mu E_0}{v_d-\gamma v_s}-\frac{1}{\tau_p}\right]. \quad (3.35)$$

The solution, Eq. (3.35), is like that of an electrostatic wave. The value of Ω rises above the linear "sound-like" value of $\gamma v_s Q$ and approaches a finite frequency at $Q=0$. This frequency is the heavy-mass plasma frequency Ω_0 modified by the ratio

$$\left\{\frac{\gamma(1+\gamma)}{[(v_d/v_s)-\gamma][2(v_d/v_s)-\gamma]}\right\}^{1/2}\left(\frac{\Delta}{X}\right)^{1/2}\approx\left(\frac{\Delta}{X}\right)^{1/2}. \quad (3.36)$$

The ratio Δ/X as pointed out before, contains effects of viscosity of the phonon distribution and the selectivity of the coupling of ac parts of the electron and phonon distributions. This solution is what one would expect from the phenomenological discussion of Sec. II, if the electron-drift velocity were always greater than the phase velocity of the solution. However, at small values of Q, this dispersion curve crosses that of α_3 and the solution is no longer valid.

A better solution, valid for small values of Q, comes from dividing by α_1, which is far from resonance for all forward traveling waves. Equation (3.24) becomes

$$\alpha_2\alpha_3+\eta\alpha_2\alpha_4+\frac{n_0Z}{X}Q\alpha_2+\beta\frac{\Delta}{X}\Omega_0^2$$
$$=i\left[-\alpha_2\frac{M}{X}\Omega_0^2+\eta\frac{\Delta}{M}\beta\alpha_4-\beta\frac{\alpha_3}{\tau_p}-\beta\frac{n_0Z}{X\tau_p}Q\right], \quad (3.37)$$

where

$$\tfrac{1}{2}(1+\gamma)<\beta=\alpha_5/\alpha_1<1. \quad (3.38)$$

Thus, β shows only slight Ω, Q dependence and can be considered constant.

Substituting Eqs. (3.25)–(3.29) into Eq. (3.37) gives

$$(1+\eta)\Omega^2-\left(v_d+\gamma v_s+\eta\gamma v_s+\eta\mu E_0-\frac{n_0Z}{X}\right)\Omega Q+\gamma v_s$$
$$\times\left(v_d+\eta\mu E_0-\frac{n_0Z}{X}\right)Q^2+\beta\frac{\Delta}{X}\Omega_0^2=i\left[\eta\frac{\Delta}{M}\beta(\Omega-\mu E_0 Q)\right.$$
$$\left.-\frac{M}{X}\Omega_0^2(\Omega-\gamma v_s Q)-\frac{\beta}{\tau_p}(\Omega-v_d Q)\right]. \quad (3.39)$$

Since $\eta\ll 1$, we may drop the terms containing η, except for those which contain $\eta\mu E_0$. A simplification can be made by letting

$$v_d'=v_d+\eta\mu E_0-(n_0Z/X); \quad (3.40)$$

and Eq. (3.39) becomes

$$\Omega^2-\left[(\gamma v_s+v_d')Q+i\left(\beta\eta\frac{\Delta}{M}-\frac{M}{X}\Omega_0^2-\frac{\beta}{\tau_p}\right)\right]$$
$$\times\Omega+v_d'\gamma v_s Q^2+\beta\frac{\Delta}{X}\Omega_0^2+i\left(\eta\frac{\Delta}{M}\mu E_0\right.$$
$$\left.-\frac{M}{X}\Omega_0^2\gamma v_s-\frac{\beta}{\tau_p}v_d+\frac{\beta n_0Z}{X}\tau_p^{-1}\right)Q=0, \quad (3.41)$$

$$\Omega=\tfrac{1}{2}(v_d'+\gamma v_s)Q\pm(\tfrac{1}{2})^{3/2}((a^2+b^2)^{1/2}+a)^{1/2}$$
$$-(i/2)\{[\Omega']\pm[(\tfrac{1}{2})^{3/2}((a^2+b^2)^{1/2}-a)]^{1/2}\}, \quad (3.42)$$

where

$$a=(v_d'-\gamma v_s)^2Q^2-4\beta\frac{\Delta}{X}\Omega_0^2-\Omega'^2, \quad (3.43)$$

$$b=2Q\left[\Omega_0^2\frac{M}{X}(v_d'-\gamma v_s)\right.$$
$$\left.-\frac{\beta}{\tau_p}(v_d'-\gamma v_s)+\beta\frac{Y}{M}2\eta\mu E_0\right], \quad (3.44)$$

$$\Omega'=\frac{M}{X}\Omega_0^2+\frac{\beta}{\tau_p}-\eta\frac{\Delta}{M}. \quad (3.45)$$

The solution, Eq. (3.42), is correct for $b>0$, which is true for $Y>\tau_p^{-1}$. There are two solutions: a higher frequency one which has only negative terms in $\mathrm{Im}(\Omega)$ and is therefore always damped, and a low-frequency solution which has positive terms in $\mathrm{Im}(\Omega)$ and is amplified. The analysis of Eq. (3.42) is simplified by setting

$$a=(v_d'-\gamma v_s)^2(Q^2-Q_0^2), \quad (3.46)$$

$$b=2(v_d'-\gamma v_s)^2CQ, \quad (3.47)$$

where

$$Q_0^2=\frac{4\beta(\Delta/X)\Omega_0^2+\Omega'^2}{(v_d'-\gamma v_s)^2}. \quad (3.48)$$

Region 1. The short-wavelength limit is defined by $Q\gg Q_0$. In this limit

$$[\tfrac{1}{2}((a^2+b^2)^{1/2}+a)]^{1/2}=(v_d'-\gamma v_s)Q-\tfrac{1}{2}(v_d'-\gamma v_s)Q_0$$
$$\times(Q_0/C)+\tfrac{1}{2}(v_d'-\gamma v_s)C(C/Q), \quad (3.49)$$

$$[\tfrac{1}{2}((a^2+b^2)^{1/2}-a)]^{1/2}=(v_d'-\gamma v_s)C+\tfrac{1}{2}(v_d'-\gamma v_s)Q_0$$
$$\times(Q_0/C)(Q_0/Q)^2. \quad (3.50)$$

The solution capable of amplification is

$$\mathrm{Re}(\Omega)=\gamma v_s Q+\tfrac{1}{4}(v_d'-\gamma v_s)(Q_0^2-C^2)(1/Q) \quad (3.51)$$

$$2\,\mathrm{Im}(\Omega)=(v_d'-\gamma v_s)C-\Omega' +\tfrac{1}{4}(v_d'-\gamma v_s)Q_0(Q_0/C)(Q_0/Q)^2. \quad (3.52)$$

Region 2. The intermediate-wavelength region where $Q\approx Q_0$. Let $Q=Q_0+q$ where $q\ll Q_0$; then the amplified solution is

$$\mathrm{Re}(\Omega)=\tfrac{1}{2}\Big[(v_d'+\gamma v_s)-\left(\frac{C}{Q_0}\right)^{1/2} \times(v_d'-\gamma v_s)\Big]Q_0+\tfrac{1}{2}\Big\{(v_d'+\gamma v_s) -\tfrac{1}{2}\Big[\left(\frac{Q_0}{C}\right)^{1/2}+\left(\frac{C}{Q_0}\right)^{1/2}\Big](v_d'-\gamma v_s)\Big\}q, \quad (3.53)$$

$$2\,\mathrm{Im}(\Omega)=(v_d'-\gamma v_s)(CQ_0)^{1/2}-\Omega' -\tfrac{1}{4}\Big[\left(\frac{Q_0}{C}\right)^{1/2}-\left(\frac{C}{Q_0}\right)^{1/2}\Big](v_d'-\gamma v_s)q. \quad (3.54)$$

Region 3. The long-wavelength region where $Q<Q_0$. Expanding to first order in Q/Q_0, the amplified solution becomes

$$\mathrm{Re}(\Omega)=\tfrac{1}{2}(v_d'+\gamma v_s)Q-\tfrac{1}{2}(v_d'-\gamma v_s)C(Q/Q_0) \quad (3.55)$$

$$2\,\mathrm{Im}(\Omega)=(v_d'-\gamma v_s)Q_0-\Omega' -[1-(C^2/Q_0^2)](v_d'-\gamma v_s)Q(Q/Q_0). \quad (3.56)$$

It can be shown that the wave is amplified in all three regions by combining the Q-independent terms in $\mathrm{Im}(\Omega)$. Equation (3.52) becomes

$$2\,\mathrm{Im}(\Omega)=2\frac{Y}{M}\frac{\beta\eta\mu E_0}{v_d'-\gamma v_s}-2\frac{\beta}{\tau_p} +\tfrac{1}{4}(v_d'-\gamma v_s)\frac{Q_0^2}{C}\left(\frac{Q_0}{Q}\right)^2, \quad (3.57)$$

which is expected to be positive for $Y/M>1/\tau_p$, i.e., whenever the phonon distribution can be excited out of equilibrium. Equation (3.56) becomes

$$2\,\mathrm{Im}(\Omega)=\left(4\beta\frac{\Delta}{X}-\Omega_0^2+\Omega'^2\right)^{1/2}-\Omega' -\left(1-\frac{C^2}{Q_0^2}\right)(v_d'-\gamma v_s)\frac{Q^2}{Q_0}, \quad (3.58)$$

in which the first two terms must be positive. The second term in Eq. (3.54) is just the geometric mean of the positive terms in Eqs. (3.52) and (3.56) and, therefore, the $\mathrm{Im}(\Omega)$ in region 2 lies between the values for regions 1 and 3. The value of $\mathrm{Im}(\Omega)$ approaches a fixed value for $Q\to 0$. At some value of Q, $\mathrm{Im}(\Omega)>\mathrm{Re}(\Omega)$, and the wavelike solutions cannot be considered modes of the system. The detailed behavior of the waves depends on the ratio C/Q_0, where

$$C/Q_0=\left(\Omega_0^2\frac{M}{X}+2\beta\frac{Y}{M}\frac{\eta\mu E_0}{(v_d'-\gamma v_s)}-\frac{\beta}{\tau_p}\right)\Big/ \left(\left[4\beta\frac{\Delta}{X}-\Omega_0^2+\left(\Omega_0^2\frac{M}{X}+\frac{\beta}{\tau_p}\right)^2\right]^{1/2}\right). \quad (3.59)$$

This ratio can be larger than one only for large Y/M. The last two terms in the numerator can be considered a measure of the net-phonon amplification by the drifting electrons, and the denominator is the frequency of the electrostatic oscillation. When this ratio is large, the phonon amplitudes become so large as to dominate the properties of the collective wave. The contribution from the first term in Eq. (3.59) is small, provided

$$\frac{\Omega_0}{[(\Delta/M)(X/M)]^{1/2}}<1 \quad \text{or} \quad \frac{\Omega_0}{[(1/\tau_p X/M)]^{1/2}}<1, \quad (3.60)$$

where Ω_0 is the natural plasma frequency of the collective system and the denominators are the geometric means of relaxation times which transfer momentum from the electrons to the phonons, and out of the phonon distribution, to either return to the electrons or be dissipated into the thermal background.

The dispersion relation for the collective electron-phonon wave can be described for various values of C/Q_0.

Case 1: $C/Q_0<1$. For $Q>Q_0$, the wave is that one described as an amplified collective-phonon wave in paper I, except that the frequency rises as $Q\to Q_0$ in a manner given by Eq. (3.51). The gain is given by Eq. (3.57), which is in close agreement with that found in paper I. For $Q\approx Q_0$, the frequency is given by Eq. (3.53), where

$$\Omega\approx\tfrac{1}{2}(v_d'+\gamma v_s)Q. \quad (3.61)$$

However, the slope of the dispersion relation can be zero or even negative. For some $Q<Q_0$, the $\mathrm{Im}(\Omega)$ becomes greater than $\mathrm{Re}(\Omega)$, and the wave solutions no longer represent modes of the system.

Case 2: $C/Q_0=1$. In this case, there is no dispersion. The solution is

$$\mathrm{Re}(\Omega)=\gamma v_s Q. \quad (3.62)$$

The lack of coupling, Eq. (3.60), or the large phonon growth rate, Eq. (3.59), causes the phonon fluctuations to dominate the collective behavior, and the electrostatic fields cannot greatly effect the wave. For some $Q<(CQ_0)^{1/2}$, the wave solutions cease to be a mode of the system.

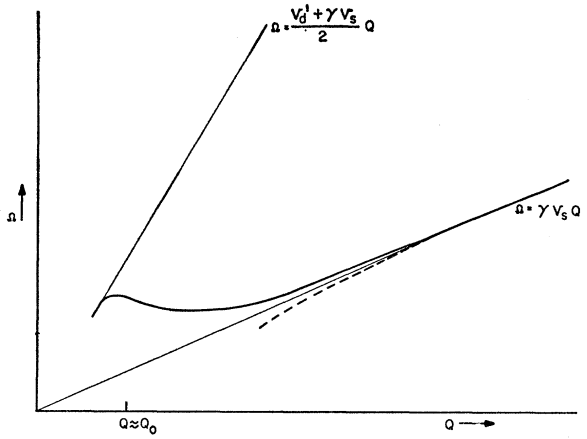

FIG. 2. The dispersion relation for collective waves. The solid line is for $C/Q_0<1$, the dotted line for $C/Q_0>1$. For $C=Q_0$, the curve would be the straight line with slope γv_s ending at cutoff. In the intermediate region $Q\approx Q_0$ the group velocity of this wave can be very small, zero, or even negative.

Case 3: $C/Q_0>1$. In this limit, the large imaginary parts of the dispersion relation cause a reduction in the real frequency below the linear value $\gamma v_s Q$. For some $Q<C$, the waves cease to be a mode of the system. The dispersion curves are diagrammed in Fig. 2.

IV. DISCUSSION AND CONCLUSION

The description in Sec. II and the analysis in Sec. III are based on plane-wave solutions in bulk matter. The observed oscillations are expected to involve wavelengths which are comparable to the size of the crystals. An exact solution of the oscillation problem would require solutions of Eqs. (3.18)–(3.21), (3.3), and boundary condition (2.1). However, one can examine the behavior of the oscillations approximately by assuming that (1) the solutions are close to plane-wave solutions, and (2) the boundary conditions select values of Q which are not very dependent on the parameters being varied. In the absence of large variations in amplitude of the collective wave (not to be confused with the changes in density which occur in a harmonic wave) along the crystal, the boundary conditions are approximately satisfied by whole wavelengths. The smallest value of Q which satisfies the boundary conditions Q' will represent the fundamental mode expected to be most strongly coupled to the external circuitry. Oscillations could occur at harmonics of this wavelength. This fundamental mode is in the long-, intermediate-, or short-wavelength region, depending on whether Q' is less, comparable to, or greater than Q_0.

Simplified versions of the collective-wave dispersion relations are diagrammed in Fig. 3. It is assumed that $\Omega_0>\Omega'$ and $C/Q_0<1$. In this figure, the frequency of the fundamental mode Q' can be found for various values of Ω_0 which is equivalent to various locations of the intermediate region. Ω_0 can be varied by varying n_0, the number of electrons. The lowest frequency solutions for a given Q' are

$$\Omega=\gamma v_s Q' \tag{4.1}$$

at the edge of the short-wavelength region. In the intermediate region, Ω changes rapidly with Ω_0. For large Ω_0, the solution is in the long-wavelength region, and

$$\Omega\approx[(v_d'+\gamma v_s)/2]Q'\approx(v_d+\gamma/2v_s)Q', \tag{4.2}$$

where it has been assumed that n_0Z/X is small. It is in the long- to intermediate-wavelength region where oscillations are most likely, because (a) the gain is greatest, and (b) the electrostatic fields which couple to the external circuitry are most important.

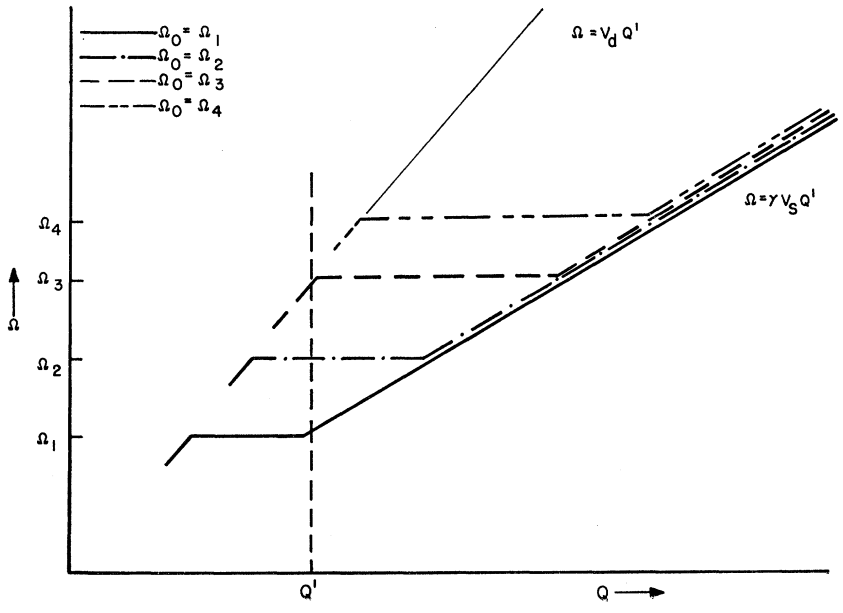

FIG. 3. A simplified dispersion relation for various values of Ω_0. The intermediate region occurs at $\Omega\approx\Omega_0$. In this region, the slope of the dispersion curve changes from $\frac{1}{2}(v_d'+\gamma v_s)\approx v_d$ to γv_s. For a fixed wave vector Q', the frequency Ω will be $\gamma v_s Q'$ for $\Omega_0\approx\Omega_1<\gamma v_s Q'$. It will rise with Ω_0 for $\Omega_0\approx\Omega_2$, where $v_d Q'>\Omega_2>\gamma v_s Q'$, and saturate at $v_d Q'$ for $\Omega_0\approx\Omega_3>v_d Q'$. At $\Omega_0\approx\Omega_4$, the wave vector Q' will be below cutoff.

Figure 4 shows simplified dispersion curves in which Ω_0 is held fixed and v_d is changed. For low values of v_d, Q' may be much less than Q_0, and the fundamental mode would fall in the region of no-wave solutions. At higher v_d, Q' comes closer to the intermediate region and spontaneous oscillations may occur. Probably, higher harmonics of the fundamental mode would occur before the fundamental in such a case.

The analysis in Paper I of the stimulated electron piezoelectric acoustic phonon interaction showed that the hot-phonon band discussed in Sec. II would extend to phonon energies

$$\hbar\omega = kT4(T_S/T)^{1/2}, \tag{4.3}$$

where

$$kT_S = \tfrac{1}{2}m^*v_s^2, \tag{4.4}$$

and k is Boltzmann's constant. The value of M in the active band below this value is

$$M = 0.126(kT)^{5/2}m^{*3/2}/\hbar^3 v_s^2. \tag{4.5}$$

Also, based on the analysis in paper I,

$$Y/X \approx \tfrac{1}{4}(v_d - v_s)/v_s. \tag{4.6}$$

In the limit $\Delta \approx Y$,

$$\Omega_0^2 = \frac{25e^2n^2\hbar^3v_s^2}{\epsilon(kT)^{5/2}m^{*3/2}}\,\frac{v_d - v_s}{v_s}. \tag{4.7}$$

When one substitutes the value appropriate to CdS into Eq. (4.7),

$$\Omega_0 \approx 10^{-8}[(v_d - v_s)/v_s]^{1/2}n_0. \tag{4.8}$$

The variation of frequency with electron density is reproduced from Ref. 1 in Fig. 5.

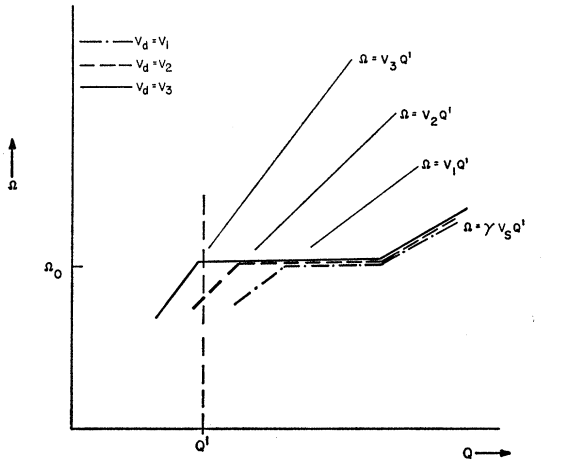

FIG. 4. A simplified dispersion curve for various values of v_d. For lowest values of $v_dQ' \approx v_1Q' < \Omega_0$, the wave with wave vector Q' will be below cutoff. For $v_dQ' \approx v_2Q' \approx \Omega_0$, the wave will exist and have $\Omega \approx v_dQ'$. At larger $v_dQ' \approx v_3Q' > \Omega_0$, the frequency rise should saturate and $\Omega \approx \Omega_0$.

The value of $n_0 \approx 10^{13} - 10^{14}$ would place the fundamental mode of the crystal in the intermediate-wavelength region. In this case, the variation of frequency with changes in n_0 could be explained by Fig. 3, which gives qualitative agreement with that observed. The lowest frequency observed corresponds to $\Omega = \gamma v_s Q'$, which is at the edge of the short-wavelength region, i.e., $\Omega_0 \approx \Omega_1$ in Fig. 3. The region of rapid change in frequency with n_0 in Fig. 5 corresponds to the change in Ω_0 in the intermediate region, i.e., $\Omega_1 < \Omega_0 < \Omega_3$ in Fig. 3. The expected variation of Ω_0 is linear in n_0 as is the experimental variation of frequency in Fig. 5. The limiting frequency should occur upon entering the long-wavelength limit, as shown in Fig. 3, which depends on the voltage through the drift velocity, as shown in Fig. 4. The re-

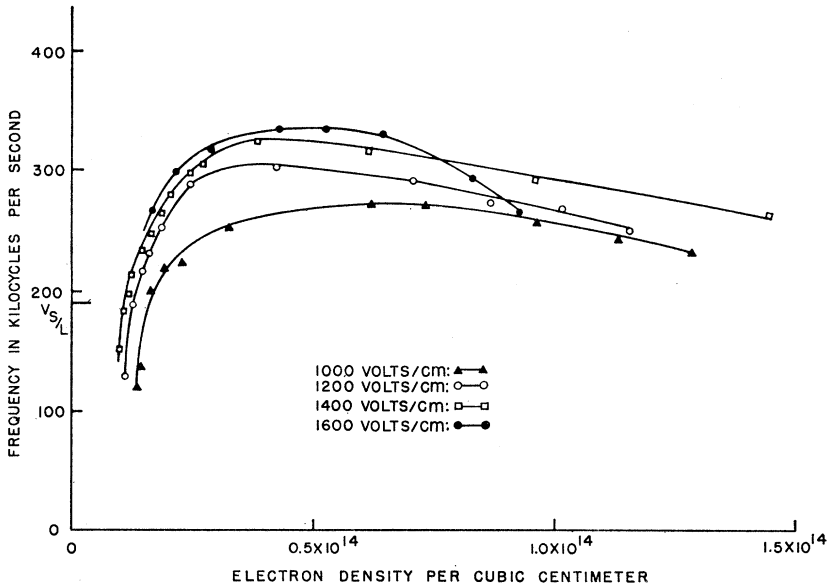

FIG. 5. Frequency of the current oscillations for the lowest frequency mode of oscillations as a function of electron density for various applied electric fields. Ambient temperature of the CdS crystal was 25±2°C.

duction in the frequency observed at largest n_0 and E_0 would be due to an increase in the ratio of C/Q_0. This brings the system close to the conditions of case 2, which lowers the frequency, as shown in Fig. 2. The increase in C/Q_0 comes from overdriving the phonon distribution, as discussed above. The quantity Y in Eq. (3.59) depends on E_0 and n_0.

The oscillations observed in GaAs may fit this analysis.[2] Larger values of n_0, smaller values of m^* and larger v_d will increase Ω_0. For $n_0 \approx 10^{14}-10^{15}$, $v_d \approx 10^7$, and $m_e^* \approx 0.02 m_e$, the value of $\Omega_0 \approx 10^9$. The fundamental mode of crystals, of the order of 10^{-1} cm, would then be in the long- to intermediate-wavelength region, and the spontaneous oscillations observed would correspond roughly to the behavior exhibited in Fig. 4.

The large drift velocities required for oscillation could be necessary to bring the fundamental mode of the crystal to the high-Q side of the cutoff, i.e., $v_d Q' \approx \Omega_0$. Similarly, the high drift velocities may be necessary before strong electron-phonon coupling occurs. The theory developed in paper I should be limited to the cases where $v_d - v_s/v_s < 1$, and the extrapolation to oscillations in GaAs, where $v_d/v_s \approx 100$, should be viewed with caution.

ACKNOWLEDGMENTS

The author wishes to thank Professor H. Ehrenreich, Dr. H. Kroger, Dr. R. W. Damon, and Dr. H. R. Carleton for many stimulating and enlightening discussions.

PHYSICAL REVIEW VOLUME 136, NUMBER 6A 14 DECEMBER 1964

Thermoelectric Size Effect in Pure Gold*

R. P. HUEBENER
Argonne National Laboratory, Argonne, Illinois
(Received 10 July 1964; revised manuscript received 13 August 1964)

The difference between the thermoelectric power of thin gold foils and a 0.010-in.-diam gold wire was measured between 77°K and room temperature. The electrical resistance difference between the foils and the wire was determined simultaneously. From the experimental results, the energy dependence of the electron mean free path and of the area of the Fermi surface in gold was obtained. Both the electron mean free path and the area of the Fermi surface decrease with increasing electron energy, which is opposite to the behavior expected from the free-electron model of a metal. The electron mean free path obtained from the resistance measurements is in agreement with the value derived from the anomalous skin effect.

I. INTRODUCTION

THE positive sign of the electronic component of the absolute thermoelectric power of the noble metals has been discussed recently in a series of theoretical papers.[1-4] The electronic component S_e^0 of the thermoelectric power depends on the way in which the area of the Fermi surface and the electron mean free path vary with the electron energy. In the free-electron model of a metal the energy dependence of both the area of the Fermi surface and the electron mean free path yield a negative term in the electronic thermoelectric power. When it was found that the Fermi surface in the noble metals is distorted and touches the zone boundaries, it was suggested[1] that the area of the Fermi surface might decrease sufficiently rapidly with increasing energy of the electrons to yield a positive electronic thermoelectric power. However, it appears today that the positive value of S_e^0 in the noble metals is caused by deviations from the free electron value of both the term containing the area of the Fermi surface and the term containing the electron mean free path.[2]

Since in the electronic thermoelectric power of a pure metal, the term containing the area of the Fermi surface and the term containing the electron mean free path always appear combined, it is usually not possible to measure each term separately. However, the term of S_e^0 containing the electron mean free path can be determined separately by measuring the effect of the specimen size on the electronic thermoelectric power. In the present investigation the influence of the specimen size on the electronic thermoelectric power is studied with high-purity gold foils in the temperature range between 77 and 296°K. From the results, the term of S_e^0 containing the electron mean free path and the term containing the area of the Fermi surface are obtained separately.

II. THEORY

The absolute thermoelectric power S^0 of a pure metal consists of a contribution S_e^0, arising from the nonequilibrium distribution of the conduction electrons, and a contribution S_g^0, caused by the interaction be-

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, England, 1960), p. 399.
[2] J. M. Ziman, Advan. Phys. **10**, 1 (1961).
[3] P. L. Taylor, Proc. Roy. Soc. (London) **A275**, 209 (1963).
[4] F. J. Blatt, Phys. Letters **8**, 235 (1964).