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Velocity of Sound in a Many-Valley Conductor

Abstract: The effect on the velocity of sound corresponding to the "Keyes effect," for nonzero frequency and finite wavelength, is calculated by means of the electron Boltzmann equation. The result may be expressed as an effective electronic contribution to the elastic constant; the deviation, χdK_0 of δK from the Keyes electronic contribution to the elastic constant, δK_0, is examined as a function of frequency and other parameters. When the Fermi velocity v is much larger than the sound velocity s and the mean free path is of the same order or larger than the acoustic wavelength, we find that $\chi \approx (s/v)^2$. When the mean free path is small compared to wavelength, $\chi = \omega^2/[\omega^2 + (\nu + 1/\bar{\tau}_d)^2]$, where ν is the intervalley scattering rate and $\bar{\tau}_d$ is an average diffusion relaxation time.

1. Introduction

This paper is concerned with the contribution to the sound velocity in many-valley conductors that is attributable to electron lattice interactions. In the presence of a static strain, ϵ, the band edge of each valley, i, is shifted by an energy $\Delta_i \epsilon$, where Δ_i is the deformation potential.[1,2] The resulting addition δK_0 to the "lattice part" of the elastic constant, K_0, was calculated by Keyes for degenerate statistics using equilibrium statistical mechanics.[3] The general form of his result is

$$\delta K_0 = -\Sigma_i g_i(E_F)[\Delta_i - \Sigma_j g_j(E_F)\Delta_j/\Sigma_r g_r]^2, \qquad (1.1)$$

where $g_i(E_F)$ is the density of states at the Fermi level in the i^{th} valley. Bruner and Keyes[4] demonstrated this effect experimentally in degenerate germanium, where the contribution can be several percent, by comparing the velocity of sound with that in undoped germanium.

Since the electron distribution may not adjust itself rapidly enough to be in adiabatic equilibrium with a time-varying strain, it is not correct a priori to calculate the sound velocity, s, from the static elastic constant by means of the equation

$$Ms^2 = K_0 + \delta K_0, \qquad (1.2)$$

where M is the mass density. Solution of the dynamical equations of motion that couple the lattice displacement to the carrier density is necessary; one replaces δK_0 in (1.2) with a δK which is in general a function of the frequency of the sound. Weinreich,[5] and Weinreich, Sanders and White,[5] have made such a calculation in terms of localized phenomenological transport relations and an equation of charge continuity. Their formulation breaks down when the applicable carrier mean free paths become comparable to or greater than the ultrasonic wavelength, a condition which occurs in pure bismuth at low temperatures. Under such conditions, the carrier distribution must be calculated from more fundamental considerations. The present paper calculates the "Keyes effect" by means of the electron Boltzmann equation.

In Sec. 2 the effective correction δK to K_0, resulting from the interaction between the carriers and the lattice strains, is found in terms of the deviations of carrier densities from equilibrium caused by the sound wave. The attenuation and sound velocity are then given by the real and imaginary parts of δK. The deviations of the carrier densities from equilibrium, to terms linear in the strain, are calculated in Sec. 3 by means of the Boltzmann equation. The resulting change in the velocity of sound is examined in detail, in Sec. 4, for the case of two non-equivalent groups of valleys.

Blount[6] has calculated the attenuation of sound in a many-valley conductor by means of the electron Boltzmann equation. For his purpose it was not necessary to consider the reaction of the carriers back on the lattice, as in the present paper, the attenuation being given directly by the rate at which the carriers absorb energy from the lattice wave.

2. Equations of motion of the lattice

The Lagrangian density of a single mode of displacement, ϕ, propagating in the x direction, can be written

$$L = \tfrac{1}{2}M(\partial\phi/\partial t)^2 - \tfrac{1}{2}K_0(\partial\phi/\partial x)^2 - \Sigma_i n_i \Delta_i\, \partial\phi/\partial x. \qquad (2.1)$$

The first term on the right of (2.1) is the kinetic energy; minus the second and third terms are, respectively, the lattice part and the electron lattice interaction part of the potential energy. The mass density, M, and the carrier densities, n_i, are both taken with respect to a volume element which is fixed in the moving lattice. The coordinate is also fixed in the lattice.

The equation of motion becomes

$$M(\partial^2/\partial t^2)\phi = K_0(\partial^2/\partial x^2)\phi + \Sigma_i\Delta_i(\partial/\partial x)n_i. \qquad (2.2)$$

Assuming that the space dependent part of n_i is linear in the strain, $\partial\phi/\partial x$, for a traveling wave,

$$\phi = \phi_0 \exp i(\omega t - kx),$$

(2.2) becomes

$$\omega^2 M\phi = k^2(K_0 + \delta K)\phi, \qquad (2.3)$$

where

$$\delta K = \Sigma_i \Delta_i C_i(k, \omega) \qquad (2.4)$$

and the C_i are defined by

$$n_i(x, t) = n_i^0 - C_i(k, \omega)ik\phi. \qquad (2.5)$$

Here n_i^0 is the equilibrium density of carriers of type i.

We can calculate the phase velocity of sound, s, and the attenuation, α, from (2.3). For $\delta K \ll K_0$,

$$\alpha = -(\omega/s_0)\tfrac{1}{2}\ \mathrm{Im}\ (\delta K/K_0) \qquad (2.6)$$

$$s = s_0[1 + \tfrac{1}{2}\,\mathrm{Re}\ (\delta K/K_0)], \qquad (2.7)$$

where s_0 is the uncorrected phase velocity.

3. Calculation of the carrier densities

We seek the time and space dependent one-electron distribution function, $f_i(\mathbf{p}, x, t)$, of a many-valley conductor in the presence of an ultrasonic wave. We shall assume degenerate statistics. The basis states whose occupation numbers we calculate are Bloch functions periodic in the unit cells of the strained lattice, the Orthogonalized Deformed Bloch functions introduced by Whitfield.[2] We assume, then, as a first approximation, that the electrons move in such a manner that their position is stationary relative to the lattice.

To first order in the strain, the energy, E_i, of an electron in an O.D.B. state of momentum $\mathbf{p}$ in valley i is

$$E_i = E_i^0(\mathbf{p}) + \Delta_i(\mathbf{p})\epsilon + q\psi^1\epsilon. \qquad (3.1)$$

The unperturbed energy E_i^0 is the energy in the absence of the strain; the energy shift due to distortion of the shape of the unit cell is $\Delta_i\epsilon$, the diagonal part of the deformation potential operator.[2] The term $\psi^1\epsilon$ is the long range electrostatic potential, arising from carrier bunching, which is not compensated by the change in ion density due to the strain.

We shall assume the Δ_i are independent of $\mathbf{p}$ and merely result in a shift of the band edge. This assumption is correct when $E_{F,i} \ll \Delta_i$, where E_{Fi} is the Fermi energy measured relative to band edge i.

The distribution function satisfies the Boltzmann equation:

$$\partial f_i/\partial t + v_{i,x}\,\partial f_i/\partial x - \partial f_i/\partial p_x(\partial/\partial x)(q\psi^1\epsilon + \Delta_i\epsilon) = -\partial f_i/\partial t|_{\mathrm{coll}}, \qquad (3.2)$$

where we have used canonical coordinates and momenta of the coordinate frame moving with the lattice.[6]

For elastic scattering of carriers, the collision term is of the form[7]

$$\partial f_i/\partial t|_{\mathrm{coll}} = \Sigma_j h^{-3}\int_j [f_j(\mathbf{p}_j')S(\mathbf{p}_j' \to \mathbf{p}_i) - f_i(\mathbf{p}_i)S(\mathbf{p}_i \to \mathbf{p}_j')]\ \delta(E_i - E_j)\ d\mathbf{p}_j', \qquad (3.3)$$

where the integration is over all momentum states in valley j, the sum is over all valleys and both spin orientations, and $S(\mathbf{p}_i \to \mathbf{p}_j') = S(\mathbf{p}_j' \to \mathbf{p}_i)$. We make the assumption that for $i = j$, $S(\mathbf{p}_i \to \mathbf{p}_j')$ depends only on the energy and is isotropic in momentum space, and for $i \neq j$, $S(\mathbf{p}_i \to \mathbf{p}_j)$ depends only on the valleys i and j. With these assumptions,

$$\partial f_i(\mathbf{p}_i)/\partial t|_{\mathrm{coll}} = -\Sigma_j \nu_{ij}(E_i)[f_i(\mathbf{p}_i) - \bar{f}_j(E_i)], \qquad (3.4)$$

where

$$\nu_{ij}(E_i) = h^{-3}S(\mathbf{p}_j \to \mathbf{p}_i)\int d\mathbf{p}_j'\ \delta(E_i - E_j) = S(\mathbf{p}_j \to \mathbf{p}_i)g_j(E_i) \qquad (3.5)$$

and

$$\bar{f}_j(E_i) = h^{-3}g_j(E_i)^{-1}\int f_j(\mathbf{p}_j')\ \delta(E_i - E_j)\ d\mathbf{p}_j'. \qquad (3.6)$$

The symbol ($\bar{\ }$) will be used to denote an average of a quantity over a constant energy surface.

We require f_i up to first power in the strain. Let us write

$$f_i = f_0[E_i^0(\mathbf{p})] + (\partial f_0/\partial E)[\Delta_i + q\psi^1 + \xi_i^1(\mathbf{p})]\epsilon + O(\epsilon^2)\cdots \qquad (3.7)$$

where ψ^1 and ξ_i^1 are independent of ϵ, and $(\partial f_0/\partial E)\xi_i^1$ represents the correction to the distribution function which arises from its lack of adiabatic equilibrium with the strain wave. Substituting (3.7) in the Boltzmann equation, (3.2), with (3.4) as the collision term and $\epsilon = \epsilon_0 \exp i(kx - \omega t)$, we get

$$i(kv_{i,x} - \omega - i/\tau_i)\xi_i^1(\partial f_0/\partial E_i^0)\epsilon = [i\omega(\Delta_i + q\psi^1) + \Sigma_j \nu_{ij}\bar{\xi}_j^1](\partial f_0/\partial E_i^0)\epsilon. \quad (3.8)$$

Here $\Sigma_j \nu_{ij} = 1/\tau_i$, the total relaxation rate, and $v_{i,x}$ is the component of the carrier velocity parallel to the propagation direction.

We now turn our attention to the equation which determines the electrostatic field $\psi^1\epsilon$. The charge density with respect to a unit volume which deforms with the lattice is calculated by integrating the terms linear in the strain on the right of (3.7) over all states, since the f_0 term is just sufficient to neutralize the ion density. The error in writing Poisson's equation in the coordinates fixed in the moving lattice instead of real space is of first power or higher in the strain and can be neglected. Thus $\psi^1\epsilon$ is determined by

$$-\epsilon_l k^2 \psi^1 \epsilon = 4\pi \Sigma_i q g_i(E_F)[\Delta_i + q\psi^1 + \bar{\xi}_i^1(E_F)]\epsilon \quad (3.9)$$

for degenerate statistics. Here ϵ_l is the lattice part of the dielectric constant.

We desire the quantities $\bar{\xi}_i^1$ and ψ^1. We can transform (3.8) into equations that involve only $\bar{\xi}_i^1$ by dividing both sides by $i(kv_{i,x} - \omega - i\tau_i^{-1})$ and integrating over all states in valley i. Thus we get

$$D_i\bar{\xi}_i^1 = [i\omega(\Delta_i + q\psi^1) - \Sigma_j \nu_{ij}\bar{\xi}_j^1], \quad (3.10)$$

where

$$D_i^{-1} = g_i^{-1}h^{-3}\int_i d\mathbf{p}_i\ \delta[E_F - E_i^0(\mathbf{p}_i)] \cdot (ikv_{i,x} - \tau_i^{-1} - i\omega)^{-1}. \quad (3.11)$$

For a spherically symmetric valley,

$$D_i = -(\tfrac{1}{2}ikv_i)\ln\left(\frac{\omega\tau_i(1 + v_i/s) - i}{\omega\tau_i(1 - v_i/s) - i}\right), \quad (3.12)$$

where v_i is the magnitude of the Fermi velocity. For an arbitrary orientation of an ellipsoidal effective mass tensor (3.12) remains unchanged; v_i becomes the Fermi velocity of an electron traveling in the direction of k.[6] We next express ψ^1 as an explicit function of ξ_i^1 by adding $-i\omega\xi_i^1$ to both sides of (3.10), multiplying by $4\pi q g_i(E_F)$, and then summing over all i. Using (3.9) and the detailed balancing principle, we get

$$\psi^1 = -\Sigma_i(i\omega q)^{-1}(\Gamma_i^2/k^2)R_i\bar{\xi}_i^1. \quad (3.13)$$

Here

$$\Gamma_i = (4\pi q^2 g_i)^{1/2}\epsilon_l^{-\frac{1}{2}} \quad (3.14)$$

and

$$D_i - \tau_i^{-1} - i\omega = R_i, \quad (3.15)$$

which will be seen to play the role of the relaxation rate due to diffusion.

With the use of (3.13) in (3.10), the equation which determines $\bar{\xi}_i^1$ becomes

$$(R_i + i\omega)\bar{\xi}_i^1 - \Sigma_j \nu_{ij}(\bar{\xi}_j^1 - \bar{\xi}_i^1) - \Sigma_j(\Gamma_j/k)^2 R_j \bar{\xi}_j^1 = -i\omega\Delta_i. \quad (3.16)$$

It is seen that Γ_i is the inverse of the Debye shielding length of carrier i. In a semimetal such as bismuth, $\Gamma \approx 10^{5\text{ to }6}$ cm^{-1}, much larger than the ultrasonic wave number, $k \approx 10^2$ cm^{-1}, at megacycle frequencies. Examination of (3.9) shows that when the electrons follow the strain adiabatically (i.e., $\bar{\xi}_i^1 = 0$), the electric potential is just sufficient to cancel the average of the deformation potential when the electrons are able to shield forces within a wavelength ($\Gamma \gg k$). Under these conditions, δK is identical with Keyes' static result, (1.1).

A study of the two-valley case will suffice to show under what conditions δK differs significantly from δK_0. For propagation of a longitudinal wave in the trigonal direction electrons and holes in bismuth may be considered as belonging to a pair of "valleys." The two-valley model also fits n-type germanium with longitudinal waves in the [111] direction.

4. The two-valley case

The solution of (3.16) in the two-valley case is

$$\bar{\xi}_i^1 = (-i\omega)Q^{-1}[\{i\omega + \nu_{21} + [1 - (\Gamma_2/k)^2]R_2\}\Delta_1 + [\nu_{12} + (\Gamma_1/k)^2 R_1]\Delta_2], \quad (4.1)$$

where

$$Q = \{i\omega + \nu_{21} + [1 - (\Gamma_2/k)^2]R_2\}\{i\omega + \nu_{12} + (1 - \Gamma_1/k)^2 R_1\} - [\nu_{12} + (\Gamma_2/k)^2 R_2][\nu_{21} + (\Gamma_1/k)^2 R_1]. \quad (4.2)$$

Interchanging the indexes 1 and 2 in (4.1) gives us $\bar{\xi}_2^1$.

$$\psi^1 = (qQ)^{-1}\{(\Gamma_1/k)^2 R_1[(i\omega + R_2 + \nu_{21})\Delta_1 + \nu_{12}\Delta_2] + (\Gamma_2/k)^2 R_2[(i\omega + R_1 + \nu_{12})\Delta_2 + \nu_{21}\Delta_1]\}. \quad (4.3)$$

In bismuth, $(k/\Gamma)^2 \ll 1$ up to microwave frequencies; therefore, we can expand all quantities in powers of this parameter and neglect all but the lowest order term. For bismuth, $\Gamma \approx K_F$; thus the Boltzmann equation approach cannot be used when $\Gamma \approx k$ and we will concern ourselves only with $k/\Gamma \ll 1$. To lowest order in $(k/\Gamma)^2$,

$$Q = -(\Gamma_1/k)^2 R_2(i\omega + \nu + R_1) - (\Gamma_2/k)^2 R_1(i\omega + \nu + R_2), \quad (4.4)$$

where $\nu = \nu_{12} + \nu_{21}$.

Using (4.4) along with our expressions for ψ^1 and $\bar{\xi}_i^1$, (4.3) and (4.2) respectively, in the expression for the particle density given by

$$n_i = n_{i,0} - g_i(E_F)(\Delta_i + \xi_i^1 + q\psi^1)\epsilon,$$

we can obtain δK from Eq. (2.4):

$$\delta K = -g_1 g_2(g_1 + g_2)^{-1}(\Delta_1 - \Delta_2)^2[1 - i\omega A], \quad (4.5)$$

where

$$A = [(g_1 + g_2)R_1R_2(g_1R_1 + g_2R_2)^{-1} + \nu + i\omega]^{-1}. \quad (4.6)$$

The factor $1 - \text{Re}(i\omega A)$ is a correction factor to the Keyes result. This is similar to the usual result $\sigma(\omega) = \sigma_0[1 - i\omega(\nu_t + i\omega)^{-1}]$ for a linear response function $\sigma(\omega)$ when one has a relaxation process. The total relaxation rate, ν_t, for our case should be equal to the real part of the first two terms in the bracket on the right side of (4.6). In the long wavelength limit, we shall find that the real part of the first term is identical with the usual relaxation rate due to diffusion; the second term is the intervalley scattering rate.

When the imaginary part of (4.5) is used to calculate the attenuation coefficient, α, using (2.6), the result is identical with the expression previously obtained by Blount.[6] We shall examine the real part of δK which determines the sound velocity in (2.7). Setting $R_i^{-1} = X_i + iY_i$, we find

$$\text{Re}\,(-i\omega A) = \frac{\omega(g_1 + g_2)(g_1 Y_2 + g_2 Y_1) - \omega^2\,|g_1/R_2 + g_2/R_1|^2}{|g_1 + g_2 + (i\omega + \nu)(g_1/R_2 + g_2/R_1)|^2}. \quad (4.8)$$

Equation (3.12) can be rewritten in order to express D_i (and hence, by (3.15), R_i) explicitly in terms of real and imaginary parts:

$$D = 2kv\Big\{\tan^{-1}(kl + \omega\tau) + \tan^{-1}(kl - \omega\tau) + \tfrac{1}{2}i\ln\left[\frac{1 + (kl)^2 + (\omega\tau)^2 + 2kl\omega\tau}{1 + (kl)^2 + (\omega\tau)^2 - 2kl\omega\tau}\right]\Big\}^{-1} \quad (4.9)$$

where $l = v\tau$, the mean free path of electrons moving in the direction of propagation of the sound. In bismuth $s/v \approx 10^{-2}$ so that (4.9), and thus (4.7), can be expressed in a power series in s/v. Keeping the lowest power of s/v,

$$X = \tau a(1 - a)^{-1} + O\left[\left(\frac{s}{v}\right)^2\right] + \cdots \quad (4.10a)$$

$$Y = \tau\frac{s}{v}\frac{kl}{(1 - a)^2}\left(a^2 - \frac{1}{1 + (kl)^2} + O\left[\left(\frac{s}{v}\right)^3\right] + \cdots\right) \quad (4.10b)$$

where $a = (kl)^{-1}\tan^{-1}(kl)$. (4.10c)

We are now in a position to examine the correction to Keyes' expression as a function of kl up to frequencies where the inverse Debye shielding length Γ becomes comparable to k, provided $s/v \ll 1$.

- 1. *Long wavelengths*

In the long wavelength limit, $kl \ll 1$, the forces on the carriers are constant between collisions, and phenomenological transport equations, together with equations of continuity, can be used to solve the problem. In this case, we can display our result in terms of the diffusion relaxation rate and an intervalley scattering rate.

$$X = 3\tau/k^2l^2 \equiv \tau_D; \quad (4.11a)$$

$$Y = \tau kls/v. \quad (4.11b)$$

The real part of R^{-1} in this limit is the diffusion relaxation time; the imaginary part is negligible. Thus

$$\text{Re}\,(-i\omega A) = -\omega^2/\{\omega^2 + [\nu + (g_1 + g_2) \times (g_1\tau_{D2} + g_2\tau_{D1})^{-1}]^2\}, \quad (4.12)$$

which is precisely what one gets from the phenomenological theory.[5]

There is the possibility of finding an appreciable correction to Keyes' result in the range $kl < 1$. The real part of $1 - i\omega A$ is the correction factor to the static value of the electron contribution to the elastic constant and sound velocity (see (4.5)). This will differ substantially from unity when $\omega \gtrsim \nu$ and $\omega\tau_D \gtrsim 1$ (see 4.12). Using (4.11a), the latter condition implies $\omega\tau \gtrsim (s/v)^2$. In order for both conditions to hold simultaneously for some value of ω, we must have $\nu\tau \gtrsim (s/v)^2$, which means that the intervalley scattering rate must be a small fraction of the total scattering rate.

- 2. *Very short wavelengths*

In the other limit, $kl \gg 1$, the exact expression is quite complicated, but we can establish an upper limit on $\text{Re}(-i\omega A)$. Expanding in powers of $1/kl$,

$$X = \tau[(\pi(kl)^{-1} + (\pi^2/3 - 1)(kl)^{-2} + \cdots] \quad (4.13a)$$

$$Y = (s/c)\tau[(\pi^2/2 - 1)(kl)^{-1} + (\pi/2)(\pi^2/4 + 1)(kl)^{-2} + \cdots]. \quad (4.13b)$$

We observe that the denominator of the right-hand side of (4.8) approaches the value $(g_1 + g_2)^2$ from above as $kl \to \infty$. The numerator becomes

$$(\pi^2/2 - 1)(g_1 + g_2)[g_2(s/v_1)^2 + g_1(s/v_2)^2] - \pi^2[g_1(s/v_2) + g_2(s/v_1)]^2. \quad (4.14)$$

Thus Re ($i\omega A$) $\approx (s/\bar{v})^2$, where $\bar{v}$ is an average Fermi velocity in the sense of (4.14). It is not surprising that the correction term Re (—$i\omega A$) is small, even at high frequencies, when one considers that the diffusion relaxation rate rises with decreasing wavelength.

• 3. *Intermediate region*

To get a feeling for the magnitude of Re ($-i\omega A$) for the intermediate range of kl, we substitute $kl = 1$ into Eqs. (4.10) and (4.8). We again find $R(-i\omega A) \approx (s/\bar{v})^2$.

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