II. MICROWAVE SPECTROSCOPY[*]

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RESEARCH OBJECTIVES

Our major emphasis is now focused on studies of the metallic and semiconducting states. This extremely broad area is one of current worldwide interest and investigation. Our specialized interest lies in interactions within the electron "plasma" and between the electron plasma and the lattice phonons. We now have considerable experience and facility in the generation and use of microwave phonons (coherent sound waves in the kilomegacycle frequency range), and, in particular, sound-attenuation measurements in metals and superconductors will be an important activity. Other studies in the microwave frequency range include surface impedance measurements (both phonon and electromagnetic impedance) and investigation of phonon amplification mechanisms in semiconductors. Related studies at optical frequencies in which a gas laser is used continue.

This program represents a continuation of the shift away from electron paramagnetic resonance in crystals which was our major interest during the past several years. A problem in paramagnetic cross relaxation which must be resolved before we can leave this area of research is described in this report. Apparatus for paramagnetic resonance measurements in solids and gases is still operative and is being used by our own personnel and by members of other laboratories.

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A. ULTRASONIC ATTENUATION IN SUPERCONDUCTING METALS AT RADIO AND MICROWAVE FREQUENCIES

This report is a summary of a Ph. D. thesis submitted to the Department of Physics, M. I. T., October 28, 1963.

Ultrasonic attenuation by conduction electrons in soft superconductors has been studied as a function of temperature, magnetic field, and frequency. A derivation is presented of the electronic contribution to the ultrasonic attenuation coefficient α_n of metals in the normal state, which follows closely the kinetic approach of Pippard[1] except that quantities involving the product of the ultrasonic frequency ω and the electronic mean-free time τ are not neglected. The same results as those obtained by Pippard are obtained for all cases in which α_n is sufficiently large to be observable. The quantum theory of superconductivity is worked out in detail by following the original Bardeen-Cooper-Schrieffer (BCS) derivation,[2] except for the introduction of the improved mathematical devices proposed by Bogolyubov[3] and Valatin.[4] In particular, the statistical operator of Valatin serves to simplify the calculation of α_s/α_n which is worked out for the case in which the phonon frequency is less than the superconducting energy gap. An analysis of ultrasonic attenuation in superconductors in the intermediate state is presented, based

upon the assumption of an average magnetization throughout the volume of the metal. Particular attention has been paid to the phenomenon of supercooling; in this research a modified form of the mathematical model of Faber[5] was followed.

Experiments were carried out at 0.165 Gc, 0.910 Gc, and 9.17 Gc. Analysis of the temperature-dependent data at 0.910 Gc indicates a close agreement with the BCS theory. The magnetic-field dependence of the ultrasonic attenuation coefficient supports the conclusions of the theoretical treatment, thereby indicating an effective demagnetizing coefficient of the sample that exhibits the proper orientation dependence, and yielding critical field values whose temperature dependence is in close agreement with the data of other investigators. The temperature dependence of the supercooling phenomenon exhibits the same sort of behavior that is anticipated from theoretical considerations, and the conclusions regarding the size of the nucleation centers that trigger the phase transition are numerically consistent with the values obtained by Faber, who employed a different experimental method. The frequency dependence of a_n agrees qualitatively with the prediction of Pippard. It was not possible to observe ultrasonic attenuation at 9.17 Gc; this is attributed to the fact that the sample faces were many wavelengths out of parallel at this frequency. Recommendations for further research are offered.

J. M. Andrews, Jr.

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B. CROSS RELAXATION IN RUBY

In 1962, certain experimental paradoxes in our measurements of cross relaxation in typical ruby maser crystals were reported.[1]

More accurate measurements have been made and have disclosed the nature of some of the discrepancies. Our original results on 0.05 per cent ruby near 27° orientation, 4400 gauss, for which 2, 3, and 4 quantum levels (Chang-Siegman notation) are equally spaced, are shown in Fig. II-1. These results are consistent with those of other experimenters, except for the presence of additional time constants as shown. At low temperatures and low chromium concentration, we have $T_2 < T_{12} < T_1$; we are referring to the time constants for spin-spin relaxation, cross relaxation, and spin-lattice relaxation, respectively. The effect of spin-spin relaxation was observable, although not plotted in Fig. II-1. If we "burn a hole" in the inhomogeneously broadened ruby
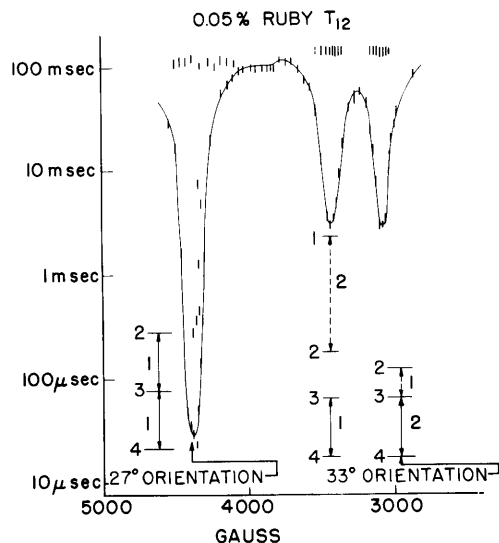
Fig. II-1. Relaxation time of ruby 3-4 transition near 30° orientation. Frequency, 9 Gc.

resonance lines with a magnetron pulse, the hole fills in within a few microseconds, and we might assume that thermal equilibrium is established within each energy level in a time of that order.

The new surprising result is that the cross relaxation is not properly describable by a time constant, but that equilibrium among the three not quite equally spaced levels is approached approximately as $t^{-1/2}$ with time. We must have a distribution of cross-relaxation times. The crystals are of laser quality and show no evidence of inhomogeneous effects in spin-lattice relaxation so that it does not seem possible to ascribe the effect to inhomogeneity in magnetic field or c-axis wander. Thus it appears that the cross relaxation proceeds between quantum levels that are not themselves in thermal equilibrium. It is true that one chromium site in the lattice differs from another in the disposition of nearest neighbors and of aluminum nuclear spins, but the observed microsecond time constant should average over the sites. Probably we have an interesting example of nonergodic behavior. The resulting theoretical puzzle is being analyzed.

R. L. Kyhl

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C. ENERGY CONSERVATION OF HYPERSONIC WAVES IN SEMICONDUCTORS

Amplification of sound waves in semiconductors through interactions with electrons drifting under the influence of a D. C. electric field and having velocity v_d greater than the velocity v_s of the sound wave was discovered some time ago.[1,2] As a coupling mechanism one may either have piezoelectric coupling or deformation potential coupling. Experiments have been successful on piezoelectric materials (CdS) at frequencies at which it is possible to work at room temperature, that is, up to 600 Mc.[3,4] For higher frequencies it is necessary to work at liquid-helium temperature. The lack of

piezoelectric semiconductors with appropriate conduction properties at these tempera-
tures makes it necessary to use the deformation potential coupling, which is much weaker
than the piezoelectric coupling, but becomes more important as the frequency increases.
Experiments at 9 Gc on n-type InSb of carrier concentration 10^{14} cm^{-3} performed in
our laboratory have not been successful thus far. We might mention, however, that
theoretically an amplification of 10 db/cm is expected at power densities described by
10 amp/20 mm^2 and 10 volts/cm. We computed also that in GaAs (piezoelectric) ampli-
fication of 70 db/cm should be possible at slightly higher power densities. But we would
require very pure samples (10^{14} cm^{-3}). We do not know whether or not these are avail-
able.

The coupling mechanism between a sound wave traveling in the z direction and
drifting electrons can be described one-dimensionally by the equations:

$$D = \epsilon E + P$$

$$T = cS + F,$$

in which D is the electric induction, E the electric field, T the stress, S the strain,
ϵ the dielectric constant, and c the elastic constant. P is a (longitudinal) polarization
and F a stress on the lattice. P and F are the coupling terms and are related by energy
relations. It is known that in piezoelectric semiconductors P = eS and F = −eE, in
which e is the piezoelectric constant. A rather simple theory[2] has been formulated for
this kind of coupling at lower frequencies. The deformation potential is described by
$P = -(C\epsilon/q)(\partial S/\partial z)$, in which C is a constant and q the electronic charge. We have
found that F has to be $-(C\epsilon/q)(\partial E/\partial z)$. This expression provides a theory for the
deformation potential which is analogous in formalism with one given by White[2] for the
piezoelectric coupling. It leads to the important result that amplification through the
deformation potential coupling in a given material under given conditions is more impor-
tant than through piezoelectric coupling at $\omega > \omega_{cr} = v_s eq/\epsilon C$, the ratio being $(\omega/\omega_{cr})^2$.
For InSb this critical frequency should be $\leqslant 10$ Gc, with e $\leqslant 0.025$ C/m^2; for GaAs, pie-
zoelectric amplification is 25 times stronger at 10 Gc; for CdS, 3600 times.

In trying to derive an expression for F, we developed some energy conservation
principles, which may have some didactical value. If a sound wave travels through a
conducting crystal, the energy appears under different forms: electromagnetic energy,
acoustical energy of the lattice, kinetic energy of the electrons and heat (incoherent
acoustical energy of the lattice). We shall try to find the relations between these dif-
ferent forms of energy. We use the following notation: E, H, D, B, ϵ, μ, international
symbols for electromagnetic fields; J, current density; P, polarization; T, stress;
S, strain; c, elastic constant; F, coupling stress; v, velocity of the electrons; v_d,
drift velocity of the electrons; u, velocity of the lattice; u_D, displacement of the lat-
tice; m_c, effective mass of the carriers; q, electronic charge; ρ, resistivity or

specific weight; N, carrier density; N_o, density of donors; E_F, Fermi energy; f, density of particles per unit volume in position and velocity space; τ, relaxation time. All fields have a D. C. term and an A. C. term of the form $\exp j(\omega t - kz)$.

1. Electromagnetic Energy

We have $D = \epsilon E + P$. From curl $E = -\mu \partial H/\partial t$ and curl $H = \frac{\partial}{\partial t}(\epsilon E + P) + J$, after dot multiplication with $-H$ and E, respectively, we obtain in the usual manner

$$-\text{div } (E \times H) = \frac{\partial}{\partial t}\left(\frac{\epsilon E^2}{2} + \frac{\mu H^2}{2}\right) + E \cdot \frac{\partial P}{\partial t} + J \cdot E. \tag{1}$$

It can be shown that for sound waves the A. C. part of div $(E \times H)$ can be neglected.

2. Coherent Motion of the Lattice

For simplicity we treat the problem one-dimensionally. We have $T = cS + F$. From $\partial T/\partial z = \rho \partial^2 u_D/\partial t^2$, with $u = \partial u_D/\partial t$ and $S = \partial u_D/\partial z$, we obtain

$$\rho \frac{\partial u}{\partial t} = \frac{\partial T}{\partial z} \qquad \text{and} \qquad \frac{\partial S}{\partial t} = \frac{\partial u}{\partial z}.$$

After multiplication with u and T, respectively, we obtain

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho u^2\right) + \frac{\partial}{\partial t}\left(\frac{1}{2}cS^2\right) + F\frac{\partial S}{\partial t} = \frac{\partial}{\partial z}(uT). \tag{2}$$

3. Kinetic Energy of the Electrons

Let us first give an introductory calculation based on the equation of motion.

$$m_c \frac{dv}{dt} = -qE - \frac{m_c(v-u)}{\tau}, \tag{3}$$

in which v is the average velocity of the electrons. We assume that τ is independent of the thermal velocity of the electrons. The assumption of completely inelastic scattering is related to the assumption $v \ll v_{th}$. This equation also assumes that the wavelength is large compared with the mean-free path, since we have not taken an integral of E over the trajectory of the particle. After taking the dot product with $Nv = Nu + N(v-u)$, we obtain

$$N\frac{d}{dt}\frac{1}{2}mv^2 = E \cdot J - \frac{m}{\tau}N(v-u)^2 - \frac{mu}{\tau}\left(\frac{J}{-q} - Nu\right)$$

$$= E \cdot J - \rho(J+Nuq)^2 + \frac{mu}{q\tau}(J+Nuq). \tag{4}$$

We made use of the expression $J = -Nqv$, we omitted the index c of m_c, and we replaced

$m/N q^2 \tau$ by the resistivity ρ. The left-hand side of this equation can be transformed to $\frac{\partial}{\partial t}\left(\frac{1}{2}mv^2 N\right) + \nabla \cdot \left(\frac{1}{2}mv^2 Nv\right)$ by making use of the facts that $v = v(r,t)$ and thus $dv/dt = (\partial v/\partial t) + v \cdot (\partial/\partial r)v$, that $N = N(r,t)$, and that the continuity equation for the number of particles is $\partial N/\partial t + \nabla \cdot (Nv) = 0$. Equation 4 thus becomes

$$\frac{\partial}{\partial t}\left(\frac{1}{2}mv^2 N\right) + \nabla \cdot \left(\frac{1}{2}mv^2 Nv\right) = E \cdot J - \rho(J+Nqu)^2 + \frac{mu}{q\tau}(J+Nqu). \tag{5}$$

The interpretation of (5) is as follows: The rate of increase per unit time of the energy density, plus the power flow from a unit volume, is balanced by the energy taken from the electromagnetic energy minus the energy lost to the scattering centers in incoherent and coherent form. The last term of the right-hand side of (5) can be understood by writing it as $u \cdot Nm(v-u)/\tau$, which is the product of the velocity of the scattering centers and the force exerted on them by the electrons.

Given Eq. 3, one can derive (5). Its interpretation is correct if v should be the real velocity of the electrons, not its average. We therefore develop a more exact calculation based on the Boltzmann transport equation in the presence of the sound wave and the D. C. electric field.

$$\frac{\partial f}{\partial t} + v \cdot \frac{\partial f}{\partial r} + \frac{-qE}{m} \cdot \frac{\partial f}{\partial v} = \frac{f_s - f}{\tau}, \tag{6}$$

with $f = f(r,v,t) =$ perturbed distribution,

$f_s =$ equilibrium distribution centered around the velocity of the scattering centers and adapted to the local electron density given by

$f_s = f_0[v-u(r,t), E_F(r,t)]$.

We now define

electron density, $N = \int f\, d^3v$

current density, $J = -\int qfv\, d^3v = -N\bar{v}q$

pressure tensor of electron gas, $\overline{\overline{P}} = \int mvvf\, d^3v$.

After integration of (6) over v-space, we get

$$\frac{\partial N}{\partial t} + \nabla \cdot (N\bar{v}) = \frac{N - N}{\tau} = 0. \tag{7}$$

We have assumed that τ and the force $(-qE/m)$ are velocity-independent. After multiplication of (6) with v and integration over v-space, we get

$$\frac{\partial}{\partial t}(N\bar{v}) + \nabla \cdot \frac{\overline{\overline{P}}}{m} - \frac{qE}{m}(-N) = \frac{Nu + J/q}{\tau}. \tag{8}$$

We made use of

$$E_i \int \frac{\partial f}{\partial v_i} v_j \, d^3v = E_i \int \frac{\partial (fv_j)}{\partial v_i} \, d^3v - E_i \int f \frac{\partial v_j}{\partial v_i} \, d^3v$$

$$= 0 - E_i \int f\delta_{ij} \, d^3v = -E_j N.$$

We shall now transform and linearize Eq. 8 in the perturbation. The index 0 will indicate the unperturbed quantities. We assume that $\int fv_i^2 \, d^3v = \frac{1}{3} \int fv^2 \, d^3v$ for $i = 1, 2, 3$, and that $\int fv_i v_j \, d^3v = 0$ for $i \neq j$. This implies that the electron gas cannot exert shear stresses; we also have neglected $\bar{v}^2$ with respect to $\overline{v^2}$, which is a second-order error. If we assume that this average $\int fv^2 \, d^3v$ is only dependent on the local position of the Fermi level, and not on other properties of the perturbation, we may set

$$\frac{P}{m} = \frac{1}{3} \int fv^2 \, d^3v = \phi(N), \tag{9}$$

so that $\nabla \cdot \overline{\overline{P}}/m = \nabla P/m = \phi'(N) \, \nabla N$. We now give an example of linearization:

$$N\bar{v} = (N_o + n)(\bar{v}_o + \tilde{\bar{v}}) = (N_o + n)\bar{v} = N_o \bar{v} + \ldots .$$

In the same way $(\partial/\partial t)(J/-q)$, $\phi'(N) \, \nabla N$, qEN/m, Nu, and $J/-q$ are replaced by $N_o \partial \bar{v}/\partial t$, $\phi'(N_o) \, \nabla N$, qEN_o/m, $N_o u$, and $N_o \bar{v}$, respectively. Thus from Eq. 8, after multiplication with m/N_o, we obtain

$$m\frac{\partial \bar{v}}{\partial t} + m \frac{\phi'(N_o)}{N_o} \nabla N = -qE + (u-v) \, m/\tau. \tag{10}$$

Dot multiplication of (10) by Nv and multiplication of (7) by $m\phi'(N_o) \, N/N_o$ and adding the results gives

$$\frac{N}{2} m \frac{\partial \bar{v}^2}{\partial t} + \frac{m\phi'(N_o)}{N_o} \left[(\nabla N) \cdot N\bar{v} + N\nabla \cdot (N\bar{v}) + \frac{1}{2} \frac{\partial N^2}{\partial t} \right] = E \cdot J - \frac{mN}{\tau} (\bar{v} - u)^2 + \frac{mu}{q\tau} (J + Nqu).$$

We now define

$$\phi'(N_o) = \frac{1}{2} v_T^2,$$

and neglect third-order, so that $N\partial \bar{v}^2/\partial t = N_o \partial \bar{v}^2/\partial t$. Then we get

$$\frac{\partial}{\partial t} \left(N_o \frac{m\bar{v}^2}{2} + \frac{mv_T^2}{4} \frac{N}{N_o} N \right) + \nabla \cdot \left(\frac{mv_T^2}{2} \frac{N}{N_o} N\bar{v} \right) = E \cdot J - \rho(J + Nqu)^2 + \frac{mu}{q\tau} (J + Nqu). \tag{11}$$

The various terms in (11) are of second order in the perturbation except the second and the third terms of the right-hand side. If we set $N = N_o + n$, we get

$$\frac{\partial}{\partial t}\left(\frac{mv_T^2}{4}\frac{N}{N_o}N\right) = \frac{\partial}{\partial t}\left(\frac{mv_T^2}{2}N + \frac{mv_T^2}{2}\frac{n^2}{2N_o^2}\right)$$

or

$$\nabla \cdot \left(\frac{mv_T^2}{2}\frac{N}{N_o}N\bar{v}\right) = \frac{mv_T^2}{2}\nabla \cdot \left(N_o\bar{v} + 2n\bar{v} + \frac{n^2\bar{v}}{N_o}\right).$$

The first-order part of (11) thus, in fact, is

$$\frac{mv_T^2}{2}\left(\frac{\partial N}{\partial t} + \nabla \cdot N_o\bar{v}\right) = 0.$$

4. Energy Balance

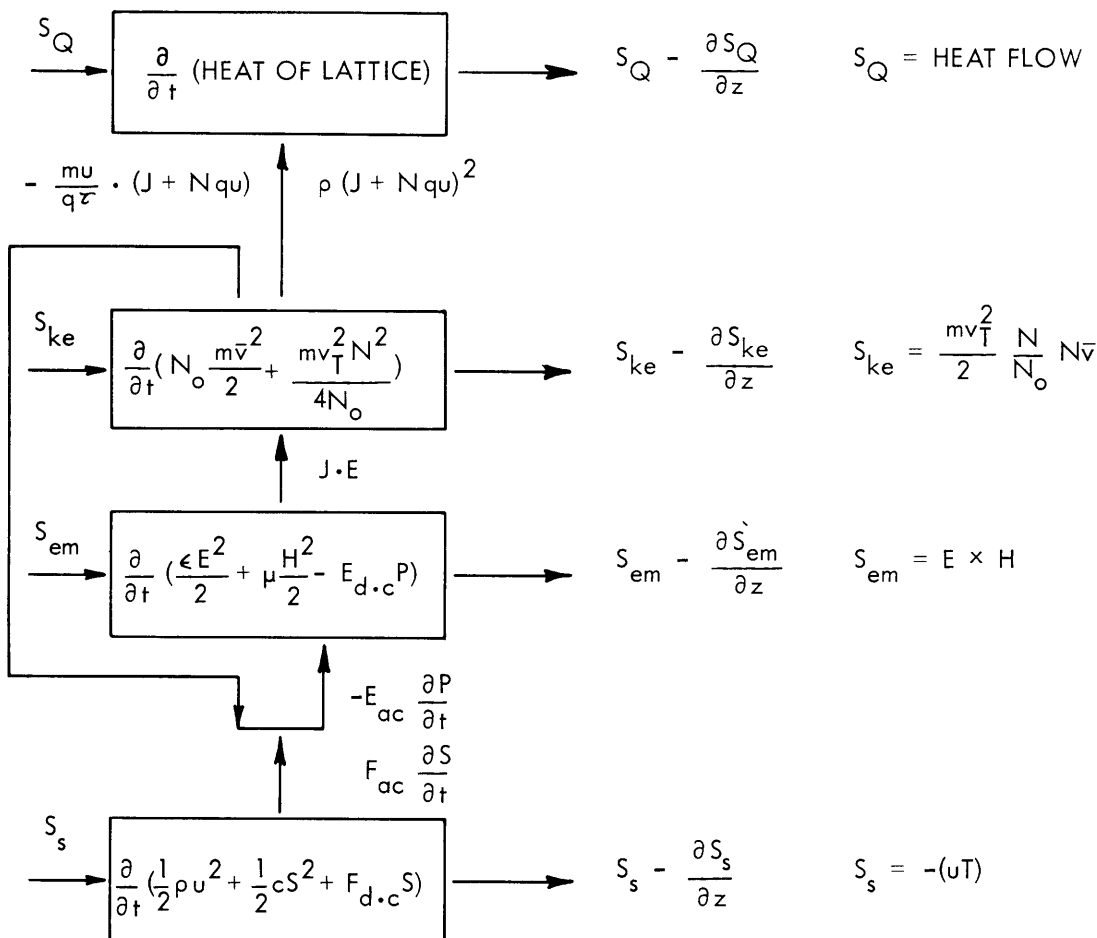From Eqs. 1, 2, and 11 we derive Fig. II-2. The electric field and the coupling

Fig. II-2. Energy balance for sound waves in semiconductors showing energy storage and power flow.

$$\langle \nabla \cdot S_Q \rangle$$

$$-\frac{mu}{q\tau}(J + Nqu) \qquad \langle \rho\,(J + Nqu)^2 \rangle$$

$$\langle \nabla \cdot S_{ke} \rangle$$

$$\langle J \cdot E \rangle = \langle J_o \cdot E_o \rangle + \langle J_{ac} \cdot E_{ac} \rangle$$

$$\langle \nabla \cdot S_{em} \rangle = -J_o \cdot E_o$$

$$\langle -E_{ac} \cdot \frac{\partial P}{\partial t} \rangle$$

$$\langle F_{ac} \cdot \frac{\partial S}{\partial t} \rangle$$

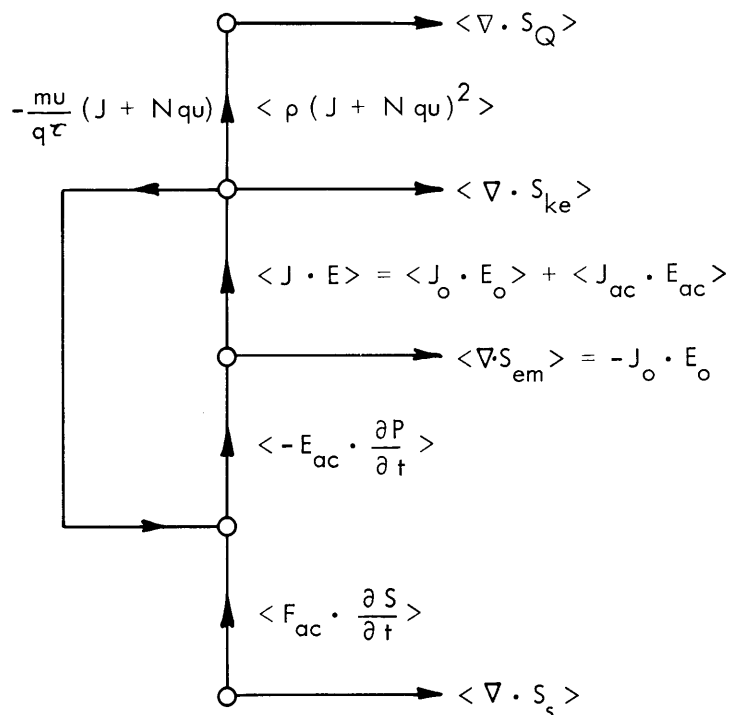$$\langle \nabla \cdot S_s \rangle$$

Fig. II-3. Energy balance for sound waves in semiconductors in a stationary situation.

stress F have been split into a D. C. and an A. C. part. Figure II-3 illustrates a stationary alternating situation, in which < > means the time average over one period. The term $\langle \nabla \cdot S_{em} \rangle$ is split into $\nabla \cdot (E_o \times H_o)$ and the contribution of the A. C. parts. The former is equal to $J_o E_o$, as can be easily understood by considering a simple conducting wire; the A. C. parts can be proved to be negligible for a sound wave. We note that $\langle \nabla \cdot S_s \rangle$ is negative for attenuation, and positive for amplification. At each small circle, we have a balance.

5. Applications

a. Equations of State: Piezoelectricity and Deformation Potential

Figure II-3 shows that

$$\left\langle F_{ac}\frac{\partial S}{\partial t} \right\rangle = \left\langle -E_{ac}\frac{\partial P}{\partial t} \right\rangle + \left\langle \frac{mu}{q\tau}(J+Nqu) \right\rangle .$$

If we neglect the second term on the right-hand side, we obtain

$$\left\langle F_{ac}\frac{\partial S}{\partial t} \right\rangle = \left\langle -E_{ac}\frac{\partial P}{\partial t} \right\rangle . \tag{12}$$

In the piezoelectric case we have $D = \epsilon E + P$, with $P = eS$. It can easily be seen that

(12) is satisfied if and only if $F_{ac} = -eE_{ac}$. There is no physical reason why this equation should be valid only for the A. C. components; thus $F = -eE$, and the equations of state thus are

$$D = \epsilon E + eS \qquad T = cS - eE.$$

We can verify the statement that $F\partial S/\partial t = -E\partial P/\partial t$, so that we can say that instantaneously the energy taken from the acoustical wave through the coupling force F shows up in the electromagnetic energy as the energy set free by the depolarization of the "piezoelectric" charges.

In the deformation-potential case, we have $D = \epsilon E + P$, with $P = -(C\epsilon/q)(\partial S/\partial z)$. By considering sinusoidal fields, we can again verify the conclusion that (12) is satisfied if and only if $F_{ac} = -(C\epsilon/q)(\partial E/\partial z)$, so that the equations of state are

$$D = \epsilon E - (C\epsilon/q)\partial S/\partial z \qquad T = cS - (C\epsilon/q)\partial E/\partial z.$$

In this case it can be verified that $F\partial S/\partial t = P\partial E/\partial t = \frac{\partial}{\partial t}(PE) - E\partial P/\partial t$, so that the previous statement about the instantaneous energy transfer is no longer true. Figure II-2 is only approximate.

b. Attenuation Constant

From Fig. II-3, we see that the energy taken from the sound wave is given by

$$Q = \left\langle F_{ac} \frac{\partial S}{\partial t} \right\rangle = \left\langle E_{ac} \frac{-\partial P}{\partial t} \right\rangle + \left\langle \frac{mu}{q\tau}(J+Nqu) \right\rangle = \left\langle J \cdot E \right\rangle + \left\langle \frac{mu}{q\tau}(J+Nqu) \right\rangle. \qquad (13)$$

If all fields are now of the form $u = u_o \exp j(\omega t - kz)$, with $jk = \alpha + j\beta$, we get

$$2\alpha \, \mathrm{Re}\left(\frac{uT^*}{2} \right) = Q \qquad (14)$$

from

$$-\left\langle \nabla \cdot S_s \right\rangle = \left\langle F_{ac} \frac{\partial S}{\partial t} \right\rangle = Q \qquad \text{and} \qquad S_s = -(uT).$$

The attenuation, α, is caused by the factor F in the equation $T = cS + F$, and thus in $\rho\partial u/\partial t = \partial T/\partial z$. If we calculate α by a first-order calculation, we use formula (14) but calculate Q and uT^* in the unperturbed situation. Thus from $\rho\partial u/\partial t = c\partial S/\partial z$, $T = cS$, and $\partial S/\partial t = \partial u/\partial z$, we get $v_s^2 = c/\rho$ and $S = u/v_s$.

Thus for α we obtain

$$\alpha = \frac{Q}{2 \, \mathrm{Re}\left(\frac{uT^*}{2} \right)} = \frac{Q}{\rho |u|^2 v_s}, \qquad (15)$$

with Q given by (13). This is the equation used in published results for calculations of a.

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