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Acoustoelectric Effect in *n*-Type Germanium

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Theory and experiment are presented for the drag exerted on electrons in a solid by a traveling ultrasonic wave. After a discussion of the reasons why the effect is generally very small, it is shown that under certain conditions in *n*-type germanium it may be quite appreciable, and that its size directly indicates the intervalley scattering rate. Experimental data are given for arsenic-doped germanium ranging in impurity content from 10^{14} to 10^{16} cm^{-3}, at temperatures from 20 to 160°K. These yield the absolute value of the "uniaxial" deformation potential constant (16 ev) and the intervalley scattering rate as a function of temperature and doping. The interpretation of the results ascribes intervalley scattering action both to phonons and to impurities. The phonon contribution yields the frequency of the $\langle 100\rangle$ longitudinal phonon (6.6×10^{12} sec^{-1}) and the size of the appropriate coupling parameter; the impurity contribution yields intervalley scattering cross sections for neutral and ionized donors as a function of temperature. The two cross sections are explained as, respectively, being due to exchange scattering events and to compound capture-reemission processes. Further analysis gives a lower limit to the valley-orbit splitting of the arsenic donor ground state (1.7×10^{-3} ev). The experiment verifies that the conduction-band valleys lie on $\langle 111\rangle$ axes at the Brillouin zone edge. Ultrasonic attenuation due to intervalley scattering is discussed and is shown to be too small to be easily measurable.

1. INTRODUCTION

THE term "acoustoelectric effect" refers to the appearance of a dc electric field along the direction of propagation of a traveling acoustic wave in a medium containing mobile charges. It is a special case of a more general phenomenon which may be called "wave-particle drag," and of which the operation of a linear accelerator and the motion of driftwood toward a beach are other examples.

Wave-particle drag will occur in steady state if there is any interaction at all between the wave and the particles (e.g., if the potential energy of the particles depends on the "displacement" which characterizes the wave), and if some dissipation mechanism is available to the particles. The latter requirement becomes evident if we think of the drag as an absorption of wave momentum. Since wave momentum and wave energy are closely related, a loss of the first must entail a loss of the second. This is not possible unless an energy sink exists.

A simple explanation of the acoustoelectric effect can be obtained by considering the following picture. With a spatially variable potential energy supplied by the wave, the particles will tend toward an equilibrium distribution which favors the regions of lower energy. The exact attainment of this distribution is, however, precluded by the fact that the wave is in motion, whereas a finite time is always required for the particles to reach equilibrium. Thus the particles will always be somewhat "behind the times." For very low values of $\omega\tau_R$, where ω is the wave frequency and τ_R the relaxation time of the distribution, the equilibrium will be almost exact; whereas for $\omega\tau_R\rightarrow\infty$ the distribution will be almost unaffected by the wave.

To find the net average force exerted by the wave on the particles, we must average the local force (i.e., the slope of the potential energy), weighting it with the local concentration of particles. For $\omega\tau_R\rightarrow\infty$, the particle distribution is uniform and the average force vanishes. It also vanishes for $\omega\tau_R\rightarrow 0$, since the distribution becomes a function of energy only. For intermediate cases, however, the electrons being "behind the times" implies a higher concentration on the forward slope than on the backward slope of the wave, entailing a net average force which is inevitably in the direction of wave propagation.

This picture shows clearly the extreme importance of the relaxation time in the process. Just what relation this time has to other properties of the particles has to be ascertained in each particular case. For the case of electrons in *n*-type germanium, we shall show that it bears a close relation to the "intervalley scattering time," that is, the mean transition time between the separate groups of states in the conduction band which lie near the minima of energy ("valleys").

It has been known for some time that the conduction band in germanium has a number of equivalent energy minima. The experiments on magnetoresistance,[1] piezoresistance,[2] and cyclotron resonance[3] leave no doubt that these minima are located on the $\langle 111\rangle$ axes of the Brillouin zone. Theoretical and experimental results[4] further favor the points at the edge of the zone, implying four equivalent valleys, rather than the eight entailed by arbitrary location on the $\langle 111\rangle$ axes. This edge position is further supported by results of the present experiment (see Sec. 8).

Although interest in the intervalley scattering rate arose early, no experiments were available that would distinguish it from the (much faster) intravalley scat-

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[1] G. L. Pearson and H. Suhl, Phys. Rev. **83**, 768 (1950).

[2] C. S. Smith, Phys. Rev. **94**, 42 (1954).

[3] Lax, Zeiger, Dexter, and Rosenblum, Phys. Rev. **93**, 1418 (1954).

[4] F. Herman, Phys. Rev. **95**, 847 (1955); Stevens, Cleland, Crawford, and Schweinler, Phys. Rev. **100**, 1084 (1955); C. Herring, *Proceedings of the International Colloqium on Semiconductors and Phosphors, Garmisch-Partenkirchen, 1956* (Interscience Publishers, Inc., New York, 1958).

tering. An exception is found in the work of Keyes,[5] whose very ingenious experiment and interpretation thereof constituted the first experimental information on this matter. It will be shown that the acoustoelectric effect provides an extremely direct measurement of the intervalley rate, involving as it does an observation of the relaxation rate of the electron distribution after a disturbance of the population of the various valleys.

The first theoretical treatment (and naming) of the acoustoelectric effect was by Parmenter,[6] who obtained results in strong disagreement with later workers. The methods which he used are, however, open to some question. Three years later another treatment was given by Van den Beukel,[7] who performed an apparently straightforward quantum-mechanical calculation which would in fact be correct if the density of electrons were extremely low and if their mean free path were much greater than an acoustic wavelength. Neither assumption is made explicitly by Van den Beukel. The first is, however, implied in his neglect of the space charge of bunched electrons, the second by his replacement of functions of the type $(\sin\omega t)/\omega$ by delta-functions. Gurevich[8] has given a calculation which somewhat parallels Van den Beukel's except that a long mean free time is explicitly assumed; but he, too, neglects space charge, and in addition appears to have taken into account absorption of ultrasonic phonons but not the accompanying stimulated emission.

Weinreich[9] has given a theoretical treatment of acoustoelectric effect for a semiconductor situation in which both electrons and holes are simultaneously involved. In this he paralleled unpublished independent work by Holstein. The point of invoking two types of carriers simultaneously was to avoid the extreme diminution of the effect produced by mutual repulsion of electrons. The suggestion that a sizable acoustoelectric voltage may appear as a result of band degeneracy, even when no minority carriers are present, was first made by Holstein.[10,11]

It is worthwhile to mention also the phenomenon of "phonon drag,"[12] which is the contribution to the thermoelectric power due to momentum transfer to electrons from thermal phonons streaming down a temperature gradient. This is qualitatively equivalent to the acoustoelectric effect; quantitatively, however, it is quite different, since the relations between typical wavelengths, mean free times, and frequencies are entirely changed.

2. GENERAL TREATMENT OF CLASSICAL WAVE-PARTICLE DRAG

We consider here the general (classical) problem of a uniform medium containing various types of particles, with the equilibrium concentration of the ith type given by n_{i0}. We imagine some type of traveling periodic wave passing through the material; let the "field strength" of the wave be denoted by Φ, so that

$$\Phi=\Phi(x-ct) \tag{2.1}$$

(we assume the wave plane, so that the problem is one-dimensional). Let Φ be so defined that Φ^2 is equal to the energy density of the field; the average power flow S is then given by

$$S=\langle\Phi^2\rangle c=\tfrac{1}{2}\Phi_0{}^2c, \tag{2.2}$$

the last expression holding for a sinusoidal wave of amplitude Φ_0, and $\langle\ \rangle$ denoting an average over a wavelength.

We now assume that there is a first-order interaction between the particles and the wave of such a nature that the ith type of particle experiences a local potential energy

$$U_i=q_i\Phi. \tag{2.3}$$

If Φ represents an acoustic wave, the constant q_i will be called the "acoustic charge."[9]

Due to the forces exerted by the wave on the particles, the local particle concentration will in general be modified. If we wish to study only the steady state, we may assume that the concentration of the ith type of particle has the form

$$n_i=n_i(x-ct). \tag{2.4}$$

We may now ask for the average (i.e., dc) force per particle, $\bar{F}_i$, exerted by the wave. Since the local force is $-q_i\partial\Phi/\partial x$, we get

$$\bar{F}_i=\langle(-q_i\partial\Phi/\partial x)n_i\rangle/\langle n_i\rangle. \tag{2.5}$$

It is instructive to calculate also the average rate at which energy is transferred from the wave to a particle. Let j_i be the particle current density of type i; then the average rate of energy transfer to a particle of this type is

$$\bar{W}_i=\langle(-q_i\partial\Phi/\partial x)j_i-q_i\Phi(\partial n_i/\partial t+\partial j_i/\partial x)\rangle/\langle n_i\rangle. \tag{2.6}$$

The second term in this expression allows for the possibility that particles of type i are not conserved; it is equal to the interaction energy removed by disappearing particles. Using the periodicity of the various quantities and the form of (2.4), we can reduce (2.6) to

$$\bar{W}_i=c\langle(-q_i\partial\Phi/\partial x)n_i\rangle/\langle n_i\rangle=c\bar{F}_i. \tag{2.7}$$

This relation could actually have been predicted

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[5] R. W. Keyes, Phys. Rev. **103**, 1240 (1956).

[6] R. H. Parmenter, Phys. Rev. **89**, 990 (1953).

[7] A. Van den Beukel, Appl. Sci. Research **B5**, 459 (1956).

[8] L. Gurevich, Bull. Acad. Sci. U.S.S.R. Phys. Ser. (English translation) **21**, 112 (1957).

[9] G. Weinreich, Phys. Rev. **104**, 321 (1956).

[10] T. Holstein (private communication).

[11] W. Sasaki and E. Yoshida, J. Phys. Soc. Japan **12**, 979 (1957), reported observing an acoustoelectric effect in n-germanium using low-frequency longitudinal waves. It later turned out, however, that the signals were really thermoelectric voltages [W. Sasaki (private communication)].

[12] H. P. R. Frederikse, Phys. Rev. **91**, 491; **92**, 248 (1953); C. Herring, Phys. Rev. **92**, 857 (1953).

from a consideration of wave dynamics alone; for since the wave carries a momentum flux equal to c^{-1} times the energy flux, the rate of loss of energy and of momentum must be related by the same factor of proportionality. Note that for a dispersive medium we must in general choose Φ to be sinusoidal in order to have it propagate without change; in this case we see that c is the *phase* velocity of the wave, in agreement with the energy-momentum relation of wave dynamics.[13]

The calculation of $n_i(x-ct)$ for a particular problem depends on the equation of motion of the particles and the forces acting on them—including their mutual repulsion (or attraction) if they are electrically charged. The last factor enters in almost all problems and merits separate consideration. Suppose that we have solved for $n_i(x-ct)$ for the case of a sinusoidal wave ($\Phi=\Phi_0 e^{ikx-i\omega t}$) without taking into account the electrostatic forces, and suppose we write the first-order result in the form

$$\delta n_i' \equiv n_i' - n_{i0} = -n_{i0}\gamma_i q_i \Phi/KT, \tag{2.8}$$

where the prime signifies that the interparticle forces were ignored. Here K is the Boltzmann constant and T the temperature; γ_i is a (complex) dimensionless number which depends on the frequency, but is in general of order unity (see Sec. 3). The correct solution δn_i will then be

$$\delta n_i = -n_{i0}\gamma_i(q_i\Phi + e_i\Psi)/KT, \tag{2.9}$$

where e_i is the *electric* charge of particle type i and Ψ is the electrostatic potential due to the particle distribution. If we assume that the medium contains enough fixed charges to neutralize the equilibrium mobile charge density $\sum_i e_i n_{i0}$, we can write

$$\nabla^2\Psi = -(4\pi/\kappa)\sum e_i \delta n_i, \tag{2.10}$$

where κ is the dielectric constant of the medium.

The correct solution for δn_i can now be obtained by substituting (2.10) into (2.9). Defining the "diminution factor" ϵ_i by

$$\delta n_i = \epsilon_i \delta n_i', \tag{2.11}$$

we obtain

$$\epsilon_i = \frac{1+\sum_j \gamma_j(\Gamma_j \lambda\!\!\!^{-})^2[1-(q_j e_i/q_i e_j)]}{1+\sum_j \gamma_j (\Gamma_j \lambda\!\!\!^{-})^2}. \tag{2.12}$$

Here $\lambda\!\!\!^{-}$ is $(2\pi)^{-1}$ times the wavelength, and Γ_j is the reciprocal of the Debye length for the jth type of particle:

$$\Gamma_j^2 \equiv 4\pi e_j^2 n_{j0}/\kappa KT. \tag{2.13}$$

We shall now mention three special cases to which Eq. (2.12) applies:

Only one type of particle.—In nearly all practical cases, $\Gamma\lambda\!\!\!^{-} \gg 1$, $\gamma \sim 1$; which yields $\epsilon \ll 1$. This is the reason why only extremely minute effects can be expected in an ordinary metal.

Bipolar semiconductor.—With both electrons and holes present, we have two types of particles with $e_1=-e_2$. This is the case treated in detail in reference 9, where the assumption $\Gamma\lambda\!\!\!^{-} \gg 1$ is made explicitly.

Symmetrical two-class system.—It will be shown in the next section that with an appropriately chosen wave in n-type germanium we have effectively two classes of particles with $n_{10}=n_{20}$, $e_1=e_2$, $q_1=-q_2$, $\gamma_1=\gamma_2$. For this case Eq. (2.12) gives

$$\epsilon_1 = \epsilon_2 = 1. \tag{2.14}$$

This is in fact the reasonable result; for since the two classes of electrons tend to bunch in exactly opposite phases, no problem of space charge arises.

3. ELECTRONS IN n-TYPE GERMANIUM

If one assumes that the valleys in the conduction band of germanium lie on $\langle 111\rangle$ axes, one can write the deformation potential energy of the αth valley as[14]

$$V^{(\alpha)} = [\Xi_d \delta_{ij} + \Xi_u K_i^{(\alpha)} K_j^{(\alpha)}] u_{ij}, \tag{3.1}$$

where u_{ij} is the strain tensor, the $K_i^{(\alpha)}$ are the components of a unit vector pointing from the center of the Brillouin zone to the αth valley, and Ξ_d and Ξ_u are two constants.

The bulk of the present experiments was conducted using an acoustic wave propagating in the $\langle 100\rangle$ direction and polarized in the $\langle 010\rangle$ direction. This leads to an effective acoustic charge for valley α, according to the definition of Sec. 2, given by

$$q^{(\alpha)} = \pm \Xi_u / 3(c_{44})^{\frac{1}{2}}. \tag{3.2}$$

The sign is determined by whether the two components $K_x^{(\alpha)}$ and $K_y^{(\alpha)}$ have the same or opposite signs. The valleys are thus divided into two classes having equal and opposite acoustic charges.

It is interesting to consider also a wave propagating in the $\langle 110\rangle$ direction and polarized in the $\langle 1\bar{1}0\rangle$ direction; in this case it is easy to verify that the deformation potential vanishes identically for all valleys. Thus for this wave there should be no acoustoelectric effect.

We now proceed to calculate the bunching that will take place as a result of the $\langle 100\rangle$-$\langle 010\rangle$ acoustic wave. Let the two classes of valleys be denoted by subscripts + and −, corresponding to acoustic charges $\pm q$. Then the two continuity equations are

$$(\partial n_\pm/\partial t) + (\partial j_\pm/\partial x) = R(\mp \rightarrow \pm), \tag{3.3}$$

where R is the rate of intervalley scattering between the indicated classes, and the current density is given by virtue of the Einstein relationship as

$$j_\pm = -D[(\partial n_\pm/\partial x) \pm (q n_\pm/KT)\partial\Phi/\partial x]. \tag{3.4}$$

Note that for motion in the $\langle 100\rangle$ direction, the diffusion constant D is equal to the directionally averaged diffusion constant ordinarily encountered.

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[13] See, for example, E. J. Post, J. phys. radium **17**, 391 (1956).

[14] C. Herring, Bell System Tech. J. **34**, 237 (1955).

Now since $q\Phi \ll KT$ for any reasonable experimental circumstances, the local equilibrium concentration of the two electron classes would, according to Boltzmann statistics, be $n_0(1\mp q\Phi/KT)$; here n_0 stands for the equilibrium value of n_+ or n_-. The rate R is determined by the amount by which the actual difference of concentrations, *viz.* $n_+ - n_-$, differs from the equilibrium difference $-2n_0 q\Phi/KT$. We thus write (assuming that the valleys are on the zone edge)

$$R(-\rightarrow +) = -R(+\rightarrow -) = -(2/3\tau) \times [n_+ - n_- + 2n_0 q\Phi/KT]. \quad (3.5)$$

Here τ is the intervalley transition time,[15] and the factor of $\frac{2}{3}$ appears because only two out of three intervalley transitions are interclass transitions. Adding the condition $n_+ + n_- = 2n_0$, we obtain

$$R(-\rightarrow +) = -(4/3\tau)[n_+ - n_0(1 - q\Phi/KT)]. \quad (3.6)$$

We may now substitute (3.6) and (3.4) into (3.3) and solve the resulting differential equation for $n_\pm$. The result for a sinusoidal wave is

$$n_\pm = n_0\left(1 \mp \frac{q\Phi_0}{KT}\frac{1}{1 - i\omega\tau_R} e^{ikx - i\omega t}\right), \quad (3.7)$$

where τ_R, the relaxation time of the distribution, is given by

$$\tau_R^{-1} = (4/3\tau) + k^2 D. \quad (3.8)$$

Equation (3.8) states the reasonable result that the relaxation of the electron distribution proceeds by two independent processes, namely intervalley scattering and spatial redistribution; the rate of the second one depends on the frequency of the acoustic wave. Direct substitution of (3.7) into (2.5) immediately yields

$$\bar{F} \equiv e\bar{E} = \frac{q^2 S}{c^2 KT}\frac{\omega^2 \tau_R}{[1 + (\omega\tau_R)^2]}, \quad (3.9)$$

where $\bar{E}$ is the effective acoustoelectric field.

4. DESIGN OF EXPERIMENT

The preceding discussion makes it clear that a measurement of acoustoelectric effect in germanium would yield relatively direct data on intervalley scattering rates. An estimate of the magnitude of the effect can be made directly from Eq. (3.9), using previously known estimates of the deformation potential.[16] One concludes that an acoustic flux of 1 watt/cm^2 at 60 Mc/sec, with the sample at liquid nitrogen temperature, will produce a field greater than one microvolt/cm if the intervalley scattering time is at least a few times 10^{-11} sec. At lower temperatures the effect should increase, not only through the explicit temperature dependence in Eq. (3.9), but also because the intervalley scattering due to phonons should drop rapidly.[14] Thus the chances of seeing the effect appeared favorable.

The basic experimental arrangement is extremely simple: a rod-shaped specimen has acoustic power injected at one end and absorbed at the other by a suitable absorber. The acoustoelectric effect should then appear as a voltage between electrodes attached at different places along the length of the rod. This is in principle a dc voltage, but because of a number of well-known reasons, it is in fact much easier to modulate the acoustic power at an audiofrequency and detect the effect by a narrow-band system tuned to this frequency.

There are two spurious sources of audio voltage that must be guarded against, since either one could easily drown out the effect under investigation: pickup and thermoelectric voltages. In connection with the first, one must consider that generation of the necessary acoustic power requires the application of approximately 30 volts rf to the transducer, while at the same time one is trying to detect microvolt signals in the immediate vicinity. One is helped, of course, by the fact that the two voltages are at different frequencies. However, a very small amount of nonlinearity in the circuit (which involves metal-semiconductor contacts) could be quite fatal. This problem was solved by careful design of the sample holder and by using a sample of special structure. A conclusive test for pickup is provided by substituting for the quartz transducer a piece of mica of equivalent capacitance. This leaves the rf current configuration, and therefore the pickup, unchanged (since the admittance of the heavily loaded transducer does not vary much through its resonance), but eliminates the acoustoelectric effect.

The possibility of thermoelectric voltages arises from the heating of the absorber by the modulated acoustic power. The ac temperature component depends strongly on modulation frequency, however, and could thus be eliminated (see below). A further test on the point is provided by changing the carrier frequency, going, for example, from the fundamental of the transducer to its first overtone. For a given acoustic power, this cannot change the thermoelectric voltages, whereas the acoustoelectric effect will vary approximately as the square of the frequency.

It was planned to measure the acoustoelectric effect as a function of temperature and also of sample doping, since intervalley scattering by impurities was expected to appear at low temperatures. A detailed description of the experiment follows.

5. EXPERIMENTAL EQUIPMENT

(a) Structure and Characteristics of Samples

Five samples were made from arsenic-doped single-crystal germanium grown in the ⟨100⟩ direction. In

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[15] This corresponds to the usual definition of intervalley scattering time, but is equal to twice the τ used in a preliminary report of this experiment: G. Weinreich and H. G. White, Phys. Rev. **106**, 1104 (1957).

[16] C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

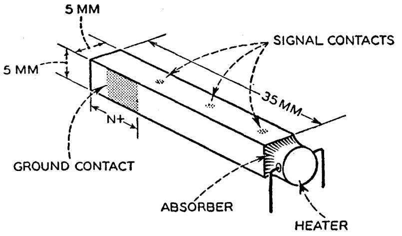

FIG. 1. Germanium specimen used for acoustoelectric measurements. "$N+$" denotes the region of high doping.

addition, one sample was grown in the ⟨110⟩ direction for the special purpose discussed in Sec. 7 (a).

In the course of growing the crystals, a large amount of arsenic was added to the melt at an appropriate point so as to produce a section of very high conductivity near the driving end (denoted by "$N+$" in Fig. 1). This was necessary since the rf current which drives the quartz transducer flows to ground through part of the germanium bar; unless this current path has a very low impedance, a considerable radio-frequency voltage may appear between the sample and ground. This voltage can then become demodulated by a nonohmic contact to the sample or other circuit nonlinearity, giving rise to a spurious signal.

The active regions of the five samples had respective room temperature resistivities of 18, 8.4, 3.4, 0.58, and 0.28 ohm-cm, which varied with temperature in the manner expected for uncompensated arsenic-doped germanium. The highly doped end region was less than 0.01 ohm-cm in all cases. The dimensions of the finished units are shown in Fig. 1. All faces were (100) crystal planes, finished with No. 600 carborundum grit. Layers of gold containing 0.1% antimony were vaporized on the units in the four areas where contacts were needed. Indium was used as the absorber of the acoustical energy being supplied to the unit by the driving transducer; the indium was alloyed to the specimen simultaneously with the evaporated gold, following which another layer of gold was evaporated to make metallic connection to the contact areas.

Finally, each finished unit was fitted with a small heater, the function of which in acoustic power measurement is described in Sec. 6. In early work the heater consisted of a small copper spool wound with fine manganin wire. Later a simpler design was adopted, which comprised a copper cylinder with a miniature carbon resistor embedded with Araldite epoxy resin in a diametrically drilled hole. In both cases the heater was soldered to the indium absorber.

(b) Transducers

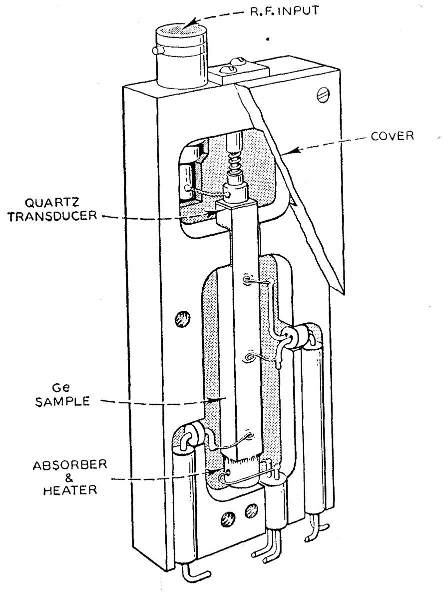

FIG. 2. Sample holder with mounted sample.

The driving transducers were quartz crystals ground to give a fundamental frequency of about 20 Mc/sec and cut so as to produce shear waves ("Y cut"). Their dimensions were 0.190 inch×0.190 inch×0.005 inch. On the side facing away from the germanium a layer of gold was evaporated which covered all but a 0.010-inch border around the edge. The other side contacted the lapped face of the germanium through a seal of Nonaq stopcock lubricant.[17]

These crystals were used successfully both in their fundamental mode and in the first overtone ($\sim$60 Mc/sec).

(c) Sample Holder

The solid copper sample holder, with its cover plate cut away, is shown in Fig. 2. It contains two separate chambers, with the germanium bar passing through a notch in the separating wall. A corrugated phosphor bronze spring fits into the thin crack between the germanium and the copper to provide a secure ground contact. Adequate mechanical strength of the joint is afforded by waxing the germanium into the notch with Apiezon "*W*" wax.

The two-chamber construction helps to isolate the output leads from the rf driving power. In addition, the fact that the germanium is supported in cantilever fashion, with only the driving end section touching the mount, is important for our method of power measurement (see Sec. 6).

The transducer is held against the germanium by a brass contact plug to which pressure is applied by a spring-loaded, Teflon-insulated plunger. The plunger assembly is removable for changing transducer or sample. The rf power enters via a type *BNC* coaxial connector, passing to the contact plug through a flexible lead.

Three channels lined with double-bore ceramic tubing conduct the three signal leads and two heater leads out

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[17] We are indebted to H. J. McSkimin for calling to our attention the usefulness of this substance as an acoustic seal.

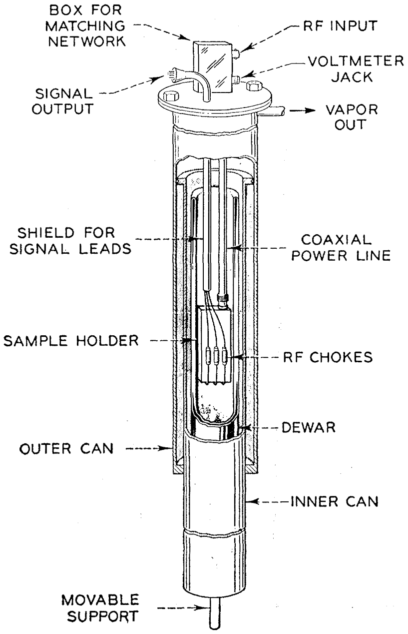

FIG. 3. Construction of cryostat.

of the main chamber. On the outside of the jig and visible in Fig. 3 are three rf chokes, one wired in series with each of the signal leads. Their purpose is to suppress picked-up rf currents which, if demodulated at the metal-semiconductor contacts, would give rise to spurious signals.

(d) Cryostat

A cryostat was required to maintain a sample at temperatures below 150°K for periods sufficiently long to permit the taking of data at each temperature. Each data point involved measurement of sample temperature, acoustic power, and acoustoelectric effect and required a time of perhaps one minute. On the other hand, a temperature determination with a precision of ± 1°K was more than adequate for the purposes of this work, so temperature drifts of the order of 1°K/minute were tolerable.

Approximately 0.25 watt of acoustical power is dissipated during a measurement. Since the efficiency of the transducers used is approximately $\frac{1}{3}$, the total electrical power input to the system is seen to be a sizable fraction of one watt. This rather high figure means that, with liquid hydrogen as refrigerant, the fact that our single Dewar is bathed in room temperature radiation merely doubles the total power input to the system. With full acoustical power input and heat conduction down the various leads and shields necessary to provide electrical connections we computed that about four hours of running with liquid hydrogen should be possible per filling of the Dewar. This estimate proved to be approximately correct.

The construction of the cryostat is shown in Fig. 3. The temperature of the sample is controlled by adjusting the level of the refrigerant relative to the sample holder by means of the telescoping tube in which the Dewar is mounted. This arrangement proved, after the experimenters had acquired some experience with it, to be entirely adequate.

Electrical connections to the sample holder were of three kinds. First, driving electrical power had to be supplied to the quartz crystal transducer. Second, electrical signals had to be obtained from various contacts to the germanium sample. Third, a thermocouple had to be used for measurement of sample holder temperature. The rf power connection to the transducers was made via a rigid coaxial line, at the bottom of which was a type *BNC* connector which engaged (and also mechanically supported) the sample holder. The outer conductor of this line was a $\frac{7}{16}$-inch o.d. thin-walled 18-8 stainless steel tube and the inner conductor a 0.020-inch silver-plated 18-8 stainless steel wire. This arrangement proved to be satisfactory, though before the inner conductor was silver-plated, rf power dissipation caused thermal expansion of the inner conductor sufficient to produce annoying variations in rf level at the transducer. Signal leads were 0.005-inch Teflon-insulated copper wire, run inside a second stainless steel tube and connected to the exterior of the cryostat via a multipin glass-to-metal lead-through. A copper-constantan thermocouple attached to the sample holder communicated with the outside of the cryostat via a length of ceramic tubing.

A shielded impedance-transforming network was placed on the cryostat top flange to match the input impedance of the rf power line to the 50-ohm transmission line from the rf generator. A coaxial receptacle was also provided for connection to a vacuum-tube voltmeter (Hewlett-Packard type 410B) with which the radio-frequency voltage at the top of the stainless steel line was monitored.

(e) Power and Measuring Circuits

A block diagram of the experimental circuitry is shown in Fig. 4. The radio-frequency source driving the transducer is modulated at an audio-frequency, and the acoustoelectric effect appears as a voltage at this frequency between two of the contacts on the sample. A low-noise amplifier and a phase-sensitive detector are used to measure the voltage from each contact to ground. The amplifier is provided with a calibrated attenuator with a range of 80 db, enabling measurement of signal strength over a wide range of amplitude; with a 1-sec time constant, a signal-to-noise ratio of unity corresponded to a signal of approximately 5×10^{-7} v rms. Low-pass filtering is provided at the amplifier input to block picked up rf signals.

Since the acoustic power is modulated, the heat generation at the absorber has an ac component, giving rise to temperature fluctuations and consequent thermoelectric voltages at the modulation frequency Ω.

It is easily shown, however, that these voltages will diminish as $\Omega^{-\frac{1}{2}}$ if measured between the heat source (absorber) and another point on the sample, and will additionally be multiplied by $\exp[-x(\Omega/2D)^{\frac{1}{2}}]$ if both contacts are at least a distance x away from the heat source (here D is the heat diffusion constant). On the other hand, the acoustoelectric effect is independent of Ω. Thus the choice of Ω is dictated by the requirement that at this frequency the ac thermoelectric voltages be negligible. The value chosen was 10 kc/sec, but it was verified that lowering Ω by a factor of 20 changed the readings by only about 5%—and that in a somewhat erratic fashion more characteristic of general apparatus noise than of systematic frequency dependence.

The rf driving power, at a frequency near 20 Mc/sec or near 60 Mc/sec, was supplied by a plate-modulated oscillator capable of producing 75 watts. This enormous excess over the power actually needed was convenient in that it made matching problems much less critical. The modulation percentage, the knowledge of which is required for computing the absolute value of the acoustoelectric effect, was measured by oscilloscopic inspection of the modulation trapezoid.

Provision was also made to connect the signal leads to a dc potentiometer for measuring thermoelectric voltages, the application of which will be discussed in the next section. Alternatively, a calibrated audio current (3.2 kc/sec) could be passed between the end contact and ground, with a tuned audio potentiometer measuring the resulting voltage between the two center contacts. This provided a sample resistivity measurement independent of thermoelectric voltages.

6. EXPERIMENTAL PROCEDURE

The acoustoelectric effect was obtained by measuring the voltage from each electrode to ground. Only differences between these voltages were considered significant, though in fact pickup was at a sufficiently low level so that the absolute voltage on the first contact was usually considerably smaller than the voltage difference between contacts. It was also verified that the sign of the voltage was such as to indicate a drag on the electrons in the direction of the wave.

With an acoustic power influx of the order of $\frac{1}{4}$ watt, a temperature difference of a few degrees exists between the active region of the sample and the copper holder. To avoid uncertainties in temperature measurement from this cause, the resistivity of the sample (calibrated against the thermocouple in the absence of acoustic power) was used as a thermometer. This method failed near the resistivity minimum that each sample experiences somewhere between 20°K and 150°K, but here a fairly reliable estimate of temperature was afforded by assuming that the temperature rise relative to the thermocouple was the same as at somewhat higher and somewhat lower temperatures.

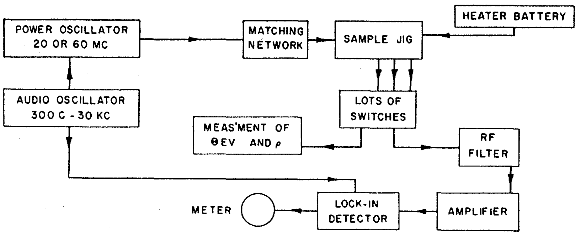

FIG. 4. Block diagram of electrical system.

The acoustic power flowing through the sample was measured by observing the dc thermoelectric voltage developed by the flow of heat from the absorber to the area near the driving end where the sample touches the copper mounting, then shutting off the rf and duplicating this thermoelectric voltage by putting dc power into the heater attached to the absorber. This is a direct substitution method and would be exact if all the rf input power were dissipated in the absorber, and/or if there were zero thermal conductance from the sample to the bath other than at the mounting point. The first hypothesis is untenable because of dissipation at the driving crystal, whereas the second is obviously also not exactly true. The result is that the heat generated at the seal causes some reverse thermal gradient along the sample, leading to an underestimate of the acoustic power and a consequent overestimate of the acoustoelectric effect. By a careful study of the thermal properties of the assembly it was found that this systematic error is of the order of 10%. The results to be reported have had this correction applied to them.

It is to be noted that although thermoelectric and acoustoelectric voltages were measured between the same contacts, the former was negligible at the modulation frequency, whereas the latter was *usually* negligible at dc. Under conditions of very large acoustoelectric effect, however, it was necessary to correct the dc potentiometer reading for it. In this connection it is important to realize that the two voltages have opposite sign.

7. RESULTS

(a) Location of Valleys

It was mentioned in Sec. 3 that for valleys with $\langle 111\rangle$ symmetry no acoustoelectric effect should appear for a shear wave propagating in the $\langle 110\rangle$ direction and polarized in the $\langle 1\bar{1}0\rangle$ direction. In order to check the experimental procedure, a special sample was made whose length was oriented in the $\langle 110\rangle$ direction, with the sides, respectively, $\langle 1\bar{1}0\rangle$ and $\langle 001\rangle$ planes. It was indeed found that no acoustoelectric voltage could be detected under the above circumstances; a 90° rotation of the transducer, which polarized the wave in $\langle 001\rangle$, immediately produced a "normal" effect (in this case $\sim$20 times noise).

If this is interpreted as an absolute null result for the $\langle 110\rangle$-$\langle 1\bar{1}0\rangle$ wave, it is interesting to ask what conclusions can be drawn from it about the location of the valleys if their ⟨111⟩ orientation is not assumed *a priori.* If the position of the valleys is taken as arbitrary, one needs not two, but six deformation-potential constants to express the energy in an arbitrary strain. It can be shown that the above null result proves that *either* the valleys are on the ⟨111⟩ axes *or* that two accidental linear relations hold between the six deformation potential constants. One might argue that such an "accidental degeneracy" is quite unlikely. In the present situation, however, the whole question is somewhat academic, since the orientation of the valleys in germanium is already established beyond any reasonable doubt.

What is perhaps a more significant result, namely that the valleys are actually at (or very close to) the Brillouin zone edge, arises from the analysis of phonon intervalley scattering in this experiment. This subject will be discussed in a later section.

(b) Deformation Potential Ξ_u

The acoustic charge q, or equivalently the deformation potential Ξ_u, appears in the expression (3.9) for the acoustoelectric field together with another unknown τ_R. The two may be obtained separately by measuring $\bar{E}$ at two frequencies. To do this it is, however, necessary to work at high enough frequencies so that the denominator term $(\omega\tau_R)^2$ is appreciable or that the diffusion term [see Eq. (3.8)] forms an appreciable contribution to τ_R. Otherwise $\bar{E}$ is simply proportional to the product $\omega^2 q^2 \tau$, and no additional information can be gained by varying the frequency.

It was found by comparing data near 20 Mc/sec and near 60 Mc/sec that the purest sample at low temperatures indeed showed a significant deviation from a ω^2 law, so that the acoustic charge could be evaluated. The result is

$$|\Xi_u| = 16 \text{ ev} \pm 10\%,$$

in good agreement with independent estimates.[16]

One may note that the deviation from an ω^2 law essentially provides an absolute calibration of the system in terms of time. Thus any systematic error in measuring the acoustoelectric effect (such as might be due to a systematic error in measuring the acoustic power, the modulation percentage, or the amplifier sensitivity) will only affect the value Ξ_u, but will leave invariant the calculated intervalley scattering times.

(c) Intervalley Scattering Rate

With q known, each experimental point can be used to compute the relaxation time τ_R. Further, since the electron diffusion constant as a function of temperature and doping is known,[18] the intervalley scattering time can be obtained from (3.8). In all but a few cases the diffusion contribution was, in fact, negligible.

Figure 5 shows the intervalley scattering rate $R \equiv \tau^{-1}$ for each of the five samples plotted as a function of temperature. It is seen that at the higher temperatures R rises with temperature, and that in this region the curves of all the samples (and especially of the purer ones) come together. We therefore attribute that part of the curve predominantly to phonon processes. On the other hand, the low-temperature rates are obviously quite different for the various samples, indicating that an impurity-dependent mechanism is in operation. We proceed now to the detailed interpretation of these curves.

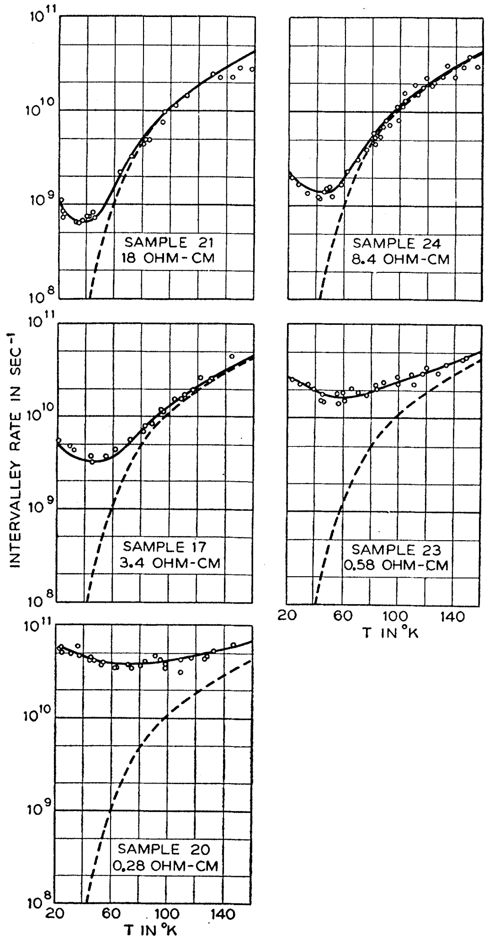

FIG. 5. Intervalley scattering rate for five samples, as a function of temperature. The circles are experimental points; the dashed line represents scattering due to phonons; the solid line includes contributions of ionized and neutral impurities.

8. INTERPRETATION: PHONON SCATTERING

If we assume that the valleys lie at the points where the ⟨111⟩ axes intersect the surface of the Brillouin zone, we find that a phonon which connects any two valleys must have a momentum vector whose terminus is at an intersection of a ⟨100⟩ axis and the surface of the zone. At this point the six phonon branches are degenerate in pairs, so that three energies are available.

For a simplified model in which only one phonon

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[18] P. P. Debye and E. M. Conwell, Phys. Rev. 93, 693 (1954).

energy is considered, the intervalley transition probability for an electron of energy ϵ above the minimum can be written[14]

$$[\tau(\epsilon)]^{-1}=w_2\left(\frac{[(\epsilon/K\Theta)+1]^{\frac{1}{2}}}{\exp(\Theta/T)-1}+\frac{[(\epsilon/K\Theta)-1]^{\frac{1}{2}}\text{ or }0}{1-\exp(-\Theta/T)}\right), \quad (8.1)$$

where $K\Theta$ is the phonon energy and w_2 is an interaction constant. The first term in the braces is for phonon absorption, the second (which is zero for $\epsilon<K\Theta$) for phonon emission. When averaged over the Boltzmann distribution, the two terms become the same, so that we obtain

$$R=2w_2\langle[(\epsilon/K\Theta)+1]^{\frac{1}{2}}\rangle_B/[\exp(\Theta/T)-1], \quad (8.2)$$

where $\langle\ \rangle_B$ denotes a Boltzmann average. In principle, the average should include the Bose denominator, since $K\Theta$ depends on the exact momentum difference between initial and final states. In fact, however, the phonon energies either leave the $\langle 100\rangle$ point with zero slope, or else in two branches of equal and opposite slope, so that to first order this consideration may be neglected. This is consistent with writing τ as a function of energy alone in the first place.

The Boltzmann average can be performed exactly, yielding

$$R=-w_2(\pi\zeta/2)^{\frac{1}{2}}H_1^{(1)}(i\zeta)\sinh\zeta, \quad (8.3)$$

where $\zeta=\Theta/2T$ and $H_1^{(1)}$ is the Hankel function. For $T\ll\Theta$, this has the asymptotic behavior

$$R\sim 2w_2\exp(-\Theta/T), \quad (8.4)$$

which is obvious from (8.2). For $T\gg\Theta$, on the other hand, R becomes proportional to $T^{\frac{3}{2}}$, which is the characteristic behavior of, for example, a simple mobility theory.

If we should try to match the "one-phonon" expression (8.3) to experimental points, we would obtain a value of Θ which is an average over the actual phonon energies, with heavy weighting of the lowest available energies (since at low temperatures these will be much more highly excited).

We find that a good match is possible using (8.3) for the high temperature portion of the purer samples. The parameters thus obtained are

$$\Theta=315^\circ\text{K}\pm 10\%,$$
$$w_2=10^{11\pm 0.3}\ \text{sec}^{-1}.$$

The curve obtained by substituting these values into (8.3) is shown as the dashed line on the graphs of Fig. 5.

The phonon energy thus obtained corresponds to a phonon frequency of $6.6\times 10^{12}\ \text{sec}^{-1}$. This is in excellent agreement with the frequency of the two degenerate longitudinal phonons obtained from neutron scattering.[19] The previously given argument would, however, lead us to expect a value close to the transverse acoustic phonon, whose energy is lower[19] by almost a factor of 3. We can understand our result by realizing that, for valleys at the zone edge, the transitions involving this low-energy phonon are forbidden.[16] The fact that we do not observe it is thus strong evidence for the existence in germanium of only four, rather than eight, valleys.

The observed value of w_2 is conveniently discussed by computing the ratio w_2/w_1, where w_1 is the coupling constant to "intravalley" phonons as defined by Herring.[14] This ratio turns out to be about 0.02. It was estimated by Herring that a value of 0.3 for this ratio is necessary to explain the deviation of the temperature dependence of electron mobility from a $T^{-\frac{3}{2}}$ law on the basis of intervalley scattering; our results therefore show that the explanation for this deviation must be sought elsewhere. This also supports the conclusion of Keyes.[5]

9. INTERPRETATION: IMPURITY SCATTERING

(a) Ionized and Neutral Impurities

The intervalley scattering not accounted for by the phonon process must be attributed to impurities. This interpretation is supported by the obvious qualitative correlation with sample doping shown by Fig. 5.

In attempting to make this interpretation quantitative over this large temperature range, the distinction between ionized and neutral donor impurities must be kept in mind. The concentration of each of these, as a function of temperature and for each sample, is known independently; the first from the resistivity and known mobilities, the second by subtraction from the asymptotic concentration of ionized donors approached at high temperatures. In these calculations the possibility of compensation was ignored, since for all samples, and down to the lowest temperature used (i.e., 20.4°K), the quantity $\log(N_+^2/N_0)$ plotted against $1/T$ showed an activation energy close to 0.0127 ev, the known ionization energy of the arsenic donors.[20] The symbols N_+ and N_0 stand, respectively, for ionized and neutral donor concentrations.

It was found not to be possible, in general, to interpret the intervalley scattering rate at a given temperature (over and above the phonon scattering) as being due to either ionized or neutral impurities alone; that is, the rate was proportional neither to N_+ nor to N_0. A good fit could be produced, however, by writing

$$R_{\text{imp}}=A(T)N_+ + B(T)N_0,$$

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[19] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

[20] T. H. Geballe and F. J. Morin, Phys. Rev. **95**, 1085 (1954).

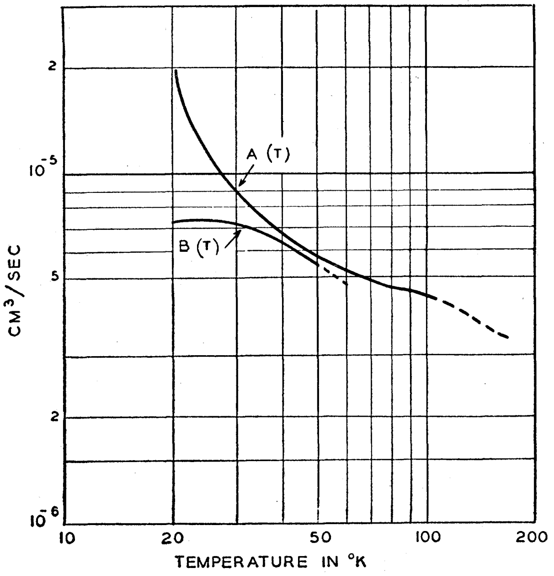

FIG. 6. Intervalley scattering rate per unit impurity concentration as a function of temperature. Curve A is for ionized arsenic donors, curve B for neutral arsenic donors.

thus matching, at a given temperature, the five samples with two parameters $A(T)$ and $B(T)$. The resulting curves are indicated in Fig. 5, while Fig. 6 shows the values of $A(T)$ and $B(T)$ thus obtained. These are to be interpreted as intervalley transition rates per unit concentration of ionized and neutral donors, respectively.

(b) Intervalley Scattering by Coulomb Field

In order to interpret these empirical factors, we must examine the available mechanisms for intervalley scattering by impurities. It is easily shown that direct scattering by the Coulomb field, which is responsible for the large (intravalley) scattering encountered in mobility theory, is negligible in the case of intervalley processes; the latter involve a very large momentum change, whereas the Coulomb field is "gentle." Thus using the plane-wave matrix elements of the Coulomb field, one estimates the ratio of intervalley to intravalley scattering by this mechanism to be $(KT/\mathcal{E}_b)^2$ where $\mathcal{E}_b$ is an energy of the order of the width of the conduction band. A numerical substitution, using intravalley rates derived from mobility, then yields an estimate orders of magnitude smaller than what we observe.

It is to be noted that the above argument applies equally to direct scattering by ionized or by neutral donors, since the very short-wavelength Fourier elements involved are independent of the shielding provided by the bound electron at or about the effective Bohr radius of the donor state.

(c) Exchange Scattering

The interpretation of the transition rate $B(T)$ involving neutral donors can be made in terms of exchange scattering. The "duration of a collision" for our case is of the order of 10^{-13} sec, and for this length of time the bound electron may be considered to be in a particular (but, of course, random) valley. If this valley differs from that of the incoming electron, and if an exchange process occurs, we have what amounts to an intervalley transition. Thus the cross section for this process should be just three-quarters of the exchange cross section.

Note that, notwithstanding the identity of the two electrons, the experiment measures a pure exchange cross section. The situation is analogous to an atomic scattering experiment in which the incoming electrons have polarized spin, only outgoing electrons with changed spin are detected, and spin-orbit interactions are negligible.

It would be interesting to use effective-mass theory to relate our observed $B(T)$, which is a Boltzmann average of the velocity–cross-section product, to exchange cross sections of electrons on atomic hydrogen. Unfortunately, not enough is known about the atomic process to make such a comparison valuable. To our knowledge no experiment has been done that would measure the exchange cross section. The available theoretical calculations for this energy range,[21] on the other hand, have used variational principles which evaluate singlet and triplet cross sections, but not the actual scattered amplitudes; thus the exchange cross section remains unknown. In addition to this, a defect in the theory is indicated by the strong disagreement with experimental measurements[22] of the total scattering.

(d) Ionized Donors: Capture and Re-Emission

We interpret the apparent intervalley scattering by ionized impurities, characterized by the rate $A(T)$, as the capture of an electron in a bound donor state followed some time later by re-emission into a new valley. This appears to be the only way in which the very small intervalley matrix elements of the Coulomb field can gain sufficient time to act. Of course, as one electron is captured to begin this process, another one nearby is re-emitted, so that from the point of view of the conduction band this constitutes an instantaneous intervalley transition.

The actual history of an electron between capture and re-emission involves a complex cascade among the various excited states. We shall not attempt to describe it in detail, but only indicate some of the simple interpretations which the data allow.

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[21] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A205**, 483 (1951).

[22] B. Bederson, Bull. Am. Phys. Soc. Ser. II, **3**, 39 (1958).

(e) Valley Changes in Ground State

As is well known,[23] the "1*s*" state of a donor in germanium consists of four levels, this number corresponding to the number of valleys in the conduction band. The four are degenerate in effective-mass approximation, but are actually split into a singlet and triplet by what we call the valley-orbit interaction. Each of these four states is a superposition of the four valleys and does not belong to any particular one. Thus "valley" is not a good quantum number unless the valley-orbit splitting vanishes.

Consequently, if we place an electron in the "1*s*" orbit and simultaneously in a known valley, it will not be in a stationary state, but in a linear combination of singlet and triplet. Since the singlet and triplet wave functions have different energies, they will change their phase in time at different rates. Thus at a later time the electron will be in a *different* linear combination of singlet and triplet, corresponding to a *different* valley (or, in general, combination of valleys). It is clear that the characteristic rate at which these changes occur is $\delta E/\hbar$, where δE is the valley-orbit splitting of the state.

It can be shown that if an electron has probability $dt/\bar{\tau}$ of leaving the state in any time interval dt, the probability that its initial and final valleys will differ is

$$\tfrac{3}{8}(\nu\bar{\tau})^2/[1+(\nu\bar{\tau})^2], \qquad (9.1)$$

where $\nu \equiv \delta E/\hbar$. That the limit of this probability for large $\nu\bar{\tau}$ is $\frac{3}{8}$, rather than $\frac{3}{4}$ (as one might expect on the basis of complete randomization of valleys), is due to the absolute phase coherence of the three component states of the triplet. In actual fact, this coherence will ultimately be destroyed by noncubic perturbations (such as vibration, including zero-point vibration, of the lattice), but for this a much longer time is required.

Let $1/\tau^*$ be the characteristic rate of electrons leaving the ground state in a valley which differs from the initial one; we then have

$$\frac{1}{\tau^*}=\frac{1}{\bar{\tau}}\times\frac{3}{8}\left(\frac{(\nu\bar{\tau})^2}{1+(\nu\bar{\tau})^2}\right)\leq\frac{3}{16}\left(\frac{\delta E}{\hbar}\right). \qquad (9.2)$$

We shall now use the last inequality in interpreting the experimental data.

(f) Magnitude of Valley-Orbit Splitting

The quantity $A(T)N_+$ gives the rate of intervalley scattering processes by ionized donors *per electron in the conduction band*. By virtue of detailed balancing, we can obtain the same rate *per captured electron* by multiplying AN_+ by N_+/N_0. Since N_+^2/N_0 is independent of doping, the new rate is too (as indeed it should be). The value of AN_+^2/N_0, as calculated from the experiment, is plotted as a function of temperature in Fig. 7.

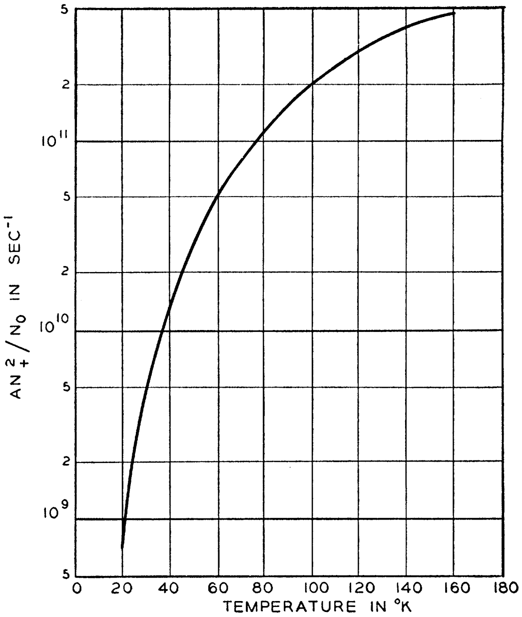

FIG. 7. Intervalley scattering rate, per electron captured on a donor, as a function of temperature (see text).

Since the valley-orbit splitting represents a failure of the effective-mass approximation, it will certainly be greatest for the state whose wave function is localized in the smallest volume, namely the ground state. It follows that the fastest way in which a captured electron can change its valley is to jump immediately to the ground state, spend only as much time there as is necessary to change valley, and immediately return to the conduction band. Any additional cascading is a "waste of time" in that it puts the electron in states of lesser valley-orbit splitting. The actual rate AN_+^2/N_0 must be smaller than this maximum rate; therefore

$$AN_+^2/N_0 \leq 1/\tau^* \leq \tfrac{3}{16}(\delta E/\hbar), \qquad (9.3)$$

where use has been made of the inequality (9.2).

We conclude that the observed data provide a lower limit on the valley-orbit splitting of the ground state. Since the largest value of AN_+^2/N_0 reached is 5×10^{11} sec^{-1}, we obtain

$$\delta E > 0.0017 \text{ ev}. \qquad (9.4)$$

(g) Capture Cross Section

The preceding discussion makes it clear that the rate $A(T)$ is a product of (a) the rate at which electrons are captured by donors and (b) the probability that, once captured, the electron will emerge in a valley which differs from its original one. The probability (b), given by (9.1), depends on the particular bound state both through its valley-orbit splitting ν and through $\bar{\tau}$, the length of time the electron spends in it. We can thus think of the rate A as being a Boltzmann average of the product of electron velocity and donor capture

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[23] W. Kohn, in *Solid State Physics* (Academic Press, Inc., New York, 1957), Vol. 5, p. 258.

cross section, provided the latter is defined to include capture processes into all states up to the excited state for which $\nu\bar{\tau}\sim 1$. Higher states will not be effective in producing intervalley transitions, since the time which an electron spends there is too short relative to the valley-orbit splitting of the state.

Now since re-emission is a thermally excited process, its rate should increase with temperature, so that warming the sample should decrease $\bar{\tau}$ for all states. It follows that as the temperature is raised, deeper-lying states are required for valley change to proceed, this being reflected in the very sharp drop of the A *versus* T curve (Fig. 6).

It is possible to make an interesting comparison of our results with the donor capture rates measured by Koenig.[24] His work was done at lower temperatures, but a rough extrapolation can be made to 20°K, with the result that our rate $A(20^\circ)$ implies a cross section some thirty times larger than his. According to the theory of Lax,[25] Koenig's cross section should include all capture processes into states which are below the continuum by $\sim KT$ or more, which at 20°K means states up to $n=3$ or so. It therefore follows that at this temperature states of considerably higher n are still effective for intervalley transitions. This is not surprising in view of the result (9.4) for the ground state and the fact that for the various hydrogen-like s orbits we may expect the valley-orbit splitting to go as n^{-3}. Presumably a more precise prediction of effective intervalley capture cross-section could be made by combining the cascade theory of Lax with the criteria outlined in the previous paragraphs.

ACKNOWLEDGMENTS

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APPENDIX: ULTRASONIC ATTENUATION BY FREE CARRIERS

It was first pointed out by Blatt[26] that the rearrangement of electrons in germanium among the various valleys under the influence of an acoustic wave can be expected to produce some attenuation of the wave. Weinreich[27] showed that this attenuation is closely related to the acoustoelectric effect; in fact, the discussion given in Sec. 2 of the present paper allows us to predict the attenuation quantitatively. Figure 8 gives this prediction for hypothetical samples of three different arsenic donor concentrations.

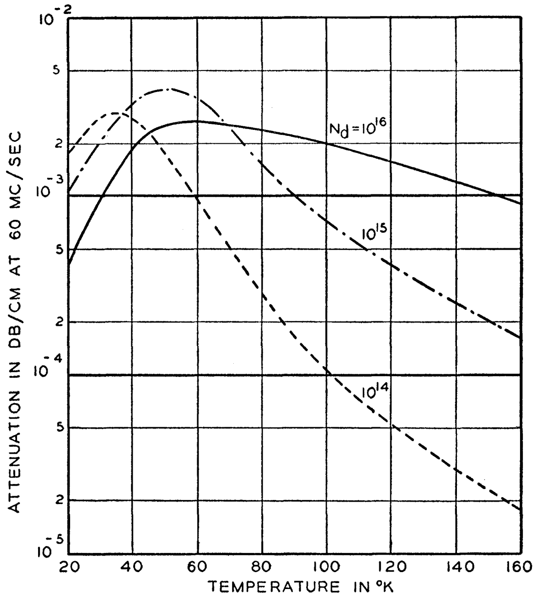

FIG. 8. Predicted acoustic attenuation due to free electrons, as a function of temperature, for three hypothetical samples of germanium. N_d is the concentration of arsenic donors.

It is to be noted that whereas the acoustoelectric effect is (for a given intervalley scattering rate) independent of the carrier concentration but proportional to the acoustic power, the attenuation coefficient is of course independent of power but proportional to the density of carriers. Thus at higher temperatures, where the intervalley scattering is due to phonons, the attenuation is highest for the highest sample doping. At intermediate temperatures, where $A(T)$ is the important contribution to R, the attenuation is approximately independent of doping, since an increase in carrier concentration causes a proportional increase in R; whereas at very low temperatures, where $B(T)$ becomes dominant, the least doped samples have the highest attenuation (since an increase in free electron concentration entails a more than proportionate increase in neutral donors).

Unfortunately, it is seen that the absolute values of attenuation are all quite small, so that an experimental measurement would be rather difficult.

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[24] S. H. Koenig, Phys. Rev. **110**, 988 (1958).

[25] M. Lax, *Proceedings of the 1958 International Conference on Semiconductors* [J. Phys. Chem. Solids **8**, 66 (1959)].

[26] F. J. Blatt, Phys. Rev. **105**, 1118 (1957).

[27] G. Weinreich, Phys. Rev. **107**, 317 (1957).