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Interaction of Microwave Phonons with Donor Electrons in Ge and Si

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It has been found that small concentrations of shallow donors in Ge and Si produce relatively large amounts of attenuation of microwave phonons at low temperatures (about 1 part per million produces about 10 dB/cm attenuation at 9 GHz). A theory is given which explains the various observed temperature, polarization, and frequency dependences of the attenuation in terms of ultrasonically induced relaxation of electrons bound to the donors. It is pointed out that such measurements can give information on the energy-level separations, symmetries, and relaxation times of bound electrons.

I. INTRODUCTION

THE attenuation of ultrasound by free carriers in semiconductors has been known for many years.[1-4] In this paper we shall describe experiments in which attenuation due to bound electrons in semiconductors was identified for the first time.[5] Some of these experimental results and a theoretical explanation were briefly presented earlier.[6]

The experiments are capable of providing information on several properties of the donors. The explanation of the attenuation involves the relaxation of electrons between bound states of the donor. This implies that there must be a considerable probability that more than one energy level is occupied. The temperature dependence of the attenuation may reflect the changing populations and therefore give information on the energy separations of the states responsible for attenuation. It may also happen that because of the symmetry of the donor wave functions, only particular kinds of strains, i.e., directions of polarizations of the ultrasound, may change the energy separations and produce attenuation. The ultrasonic method may therefore be useful in determining the symmetries of donor wave functions. Another result of these studies is the measurement of relaxation times of electrons among energy levels of donors; for some donors this may be the only method presently available.

II. EXPERIMENTAL METHOD

The experiments were measurements of the attenuation of 3- and 9-GHz ultrasonic waves as a function of temperature. The method used was described more fully elsewhere.[7] Basically, the power in an ultrasonic echo was compared to the power at 4°K, and changes were recorded as the temperature was slowly increased from 4°K. The temperature was measured by a Au-Co thermocouple in contact with the sample. The ultrasonic transducer was an evaporated Ni-Fe film which was in ferromagnetic or spin-wave resonance. This required that a magnetic field of approximately 7 kG be applied to the sample. The Zeeman splitting of the donor spin, however, plays no role in the observed effects.

The germanium samples were grown in this laboratory by C. J. Lent. The P-doped Si was purchased from Dow Corning, and the Li-doped Si was kindly lent to us by Dr. G. Watkins, who originally obtained it from Dr. A. K. Ramdas. The donor concentrations in the Ge were established by measuring the resistivity at room temperature, and comparing this to the known curves of resistivity versus concentration. For the Si samples, Hall-effect measurements were also made. The samples were x-ray oriented to ±0.5°, cut and mechanically polished to optical tolerances.

III. EXPERIMENTAL RESULTS IN *n*-TYPE Ge

The measured attenuation as a function of temperature of shear waves propagating in the [100] direction of Ge is shown by the solid curves of Fig. 1. The donors are Sb, P, and As in concentration of about 3×10^{15}/cc. The ultrasonic frequency was 9.0 GHz. The attenuation of the transverse wave in [100] undoped[7] Ge is also shown. The differences between the doped and undoped curves are the effects of the dopants. The longitudinal wave in the [100] direction in these samples had about the same attenuation as in pure Ge.

Measurement of the attenuation of microwave ultrasound has always been plagued by the nonexponential decay of the echoes (beating effects). The procedure used by us and others to measure the attenuation is to observe changes in attenuation with temperature. The absolute magnitude of the attenuation α is established by assuming a reasonable value at some temperature, e.g., that $\alpha=0$ at $T=4$°K. This obviously cannot be the case in Sb-doped Ge since the attenuation decreases as the temperature increases above 4°K. The procedure

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[1] H. D. Nine, Phys. Rev. Letters **4**, 359 (1960).

[2] Nonpiezoelectric crystals: M. Pomerantz, R. W. Keyes, and P. E. Seiden, Phys. Rev. Letters **9**, 521 (1962).

[3] W. P. Mason and T. Bateman, Phys. Rev. **134**, A1387 (1964).

[4] For reviews of ultrasonic effects in semiconductors see N. Einspruch, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1965), Vol. 17, p. 217; and Ref. 6.

[5] The attenuation of sound in B-doped Si reported in Ref. 3 was probably due to bound carriers for acceptor densities $<10^{18}$/cc. It was attempted to explain the results as a free-carrier effect.

[6] M. Pomerantz, Proc. IEEE **53**, 1438 (1965); in Proceedings of Sendai Symposium on Acoustoelectronics, Tohoku University, Sendai, Japan, 1968 (unpublished).

[7] M. Pomerantz, Phys. Rev. **139**, A501 (1965).

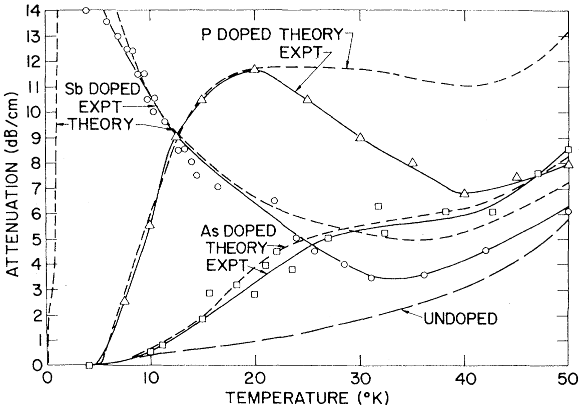

FIG. 1. Temperature dependence of the attenuation of 9-GHz shear waves propagating in the [100] direction in n-type Ge and pure Ge. The donor concentrations are, for Sb, $N\approx 2\times 10^{15}$/cc; for P, $N\approx 4\times 10^{15}$/cc; for As, $N\approx 3\times 10^{15}$/cc. The theoretical curves are plots of Eq. (6), using one value of τ for each curve that gives the best fit. The dashed curve is the attenuation in pure Ge.

we have used to obtain the absolute magnitudes of α is to fit the observed $\Delta\alpha(T)$ to the known values of $\alpha(T)$ of pure Ge at higher temperatures with an additional correction for attenuation due to free carriers. Thus we[7] have measured the attenuation of the transverse wave in the [100] direction of pure Ge to be 6 dB/cm at 50°K. To correct for the effect of free electrons released from the donors in doped samples, we calculated the electronic attenuation given by[2,3]

$$\alpha_e = (n\Xi_u^2\beta/18cv)\omega\tau/(1+\omega^2\tau^2)\,, \tag{1}$$

where n is the density of free electrons, Ξ_u is the shear deformation potential constant which is 17 eV for Ge, $\beta=1/kT$ is the inverse of the absolute temperature multiplied by the Boltzmann constant, ω is the circular frequency, τ is the electron relaxation time given by[8]

$$\tau^{-1}=\tau_{\text{iv}}^{-1}+D\omega^2/v^2$$

where τ_{iv} is the intervalley scattering time, D is the diffusion constant, v is velocity of the shear wave, and c is the elastic constant of the wave. The formula of Eq. (1) is applicable to nondegenerate electron gases, which is appropriate for the temperatures (≈ 50°K) and concentrations ($<10^{16}$/cc) we shall use. Intervalley relaxation rates τ_{iv}^{-1} have been determined from the acoustoelectric effect[8,9] to be of the order of $\lesssim 10^{+10}$ sec^{-1} for $N_e\approx 10^{15}$/cc, at 50°K. The diffusion constant may be found from the Einstein relation $D=\mu/\beta e$, where values of the mobility as function of temperature and concentration are known.[10] The relaxation rate due to diffusion for $N\approx 3\times 10^{15}$ at $T=50$°K then turns out to be $\approx 10^{12}$ sec^{-1} at 9 GHz. We thus find for the attenuation due to free carriers, for the concentrations of donors in Fig. 1, $\alpha_e(\text{Sb})=0.2$ dB/cm, $\alpha_e(\text{P})=0.4$ dB/cm, and $\alpha_e(\text{As})=0.3$ dB/cm, at $T=50$°K. The total attenuation at 50°K is thus the lattice attenuation (6 dB/cm) plus the electronic attenuations, or approximately 6–7 dB/cm.

The above discussion shows that at 50°K the attenuation due to free carriers is negligible; it is less than our experimental error. At lower temperatures the carriers freeze out onto the donors with an exponential temperature dependence, and their effect is further reduced. Thus it may be concluded that free carriers are not responsible for the excess attenuation observed at low temperature. We shall give a theory in Sec. IV that explains the attenuation in the low-temperature region as being due to the electrons that are bound to the donors. In addition to explaining the large magnitude of the excess attenuation for such small concentrations, this theory also explains the experimental observations that (i) the attenuation versus temperature is much different for different chemical species of the donors and (ii) the largest excess attenuations are for the ultrasonic modes whose elastic constants $c=\rho v^2$ contains c_{44}.

The frequency dependence of the attenuation was measured by repeating measurements of α versus T at 3 GHz. The results are shown in Fig. 2. Note that the concentration of As is higher than in Fig. 1. It was found that the temperature dependence of the attenuation is about the same as at 9 GHz but that the magnitudes are lower by a factor of about 3 at 3 GHz than they are at 9 GHz.

IV. THEORY OF ULTRASONIC ATTENUATION BY NEUTRAL DONORS AND ITS COMPARISON TO EXPERIMENT

It is clear from the preceding estimates that the magnitude (and temperature dependence) of the excess attenuation observed in the doped Ge at low temperatures cannot be explained by attenuation by free electrons. The possibility that bound electrons could strongly scatter phonons was first recognized by R. W. Keyes.[11] He applied P. J. Price's theory[12] of the effect of strain on the bound states of donors to the scattering of thermal phonons. Price's theory is based in turn on the model of the hydrogenlike states of electrons bound to donors, which has been developed mostly by Kohn and Luttinger.[13]

In this model the electrons are bound to the donor by the Coulomb force, as modified by the dielectric constant of the medium (for large orbits) and the use of the effective-mass approximation. In the case of multivalley bands the bound states will generally be orbitally degenerate. The lowest conduction bands of Ge, in particular, are fourfold degenerate. The theory

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[8] G. Weinreich, T. M. Sanders, and H. G. White, Phys. Rev. **114**, 33 (1959).

[9] G. Weinreich and B. Tell, Phys. Rev. **143**, 584 (1966).

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

[11] R. W. Keyes, Phys. Rev. **122**, 1171 (1961).

[12] P. J. Price, Phys. Rev. **104**, 1223 (1956).

[13] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 5, p. 257.

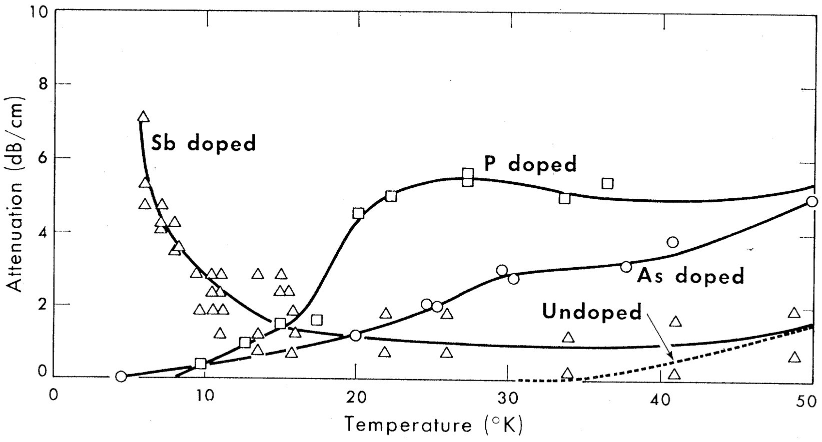

FIG. 2. Temperature dependence of the attenuation of 3-GHz shear waves propagating in the [100] direction of n-type and pure Ge. The donor concentrations are, for Sb, $N\approx 2\times 10^{15}$/cc; for P, $N\approx 4\times 10^{15}$/cc; for As, $N\approx 8\times 10^{15}$/cc. The dashed curve is the attenuation in pure Ge.

of Kohn and Luttinger predicts that the ground state of a donor in Ge will thus be a fourfold degenerate 1s state. Local fields about the impurity will lift this degeneracy, and produce threefold and nondegenerate states. These are referred to as the 1s (T_1) and 1s (A_1), respectively, indicating their group theoretical transformation properties. The splitting between the singlet and triplet states is known as the "chemical shift" or "valley-orbit" splitting; its magnitude[14] 4Δ is different for different donors, and several are listed in Table I. It has been found for all shallow donors in Ge that the singlet is lowest in energy.

Price[12] calculated the effect of strain on the ground states of the donor. His result for a shear in the (100) plane is shown in Fig. 3. It is seen that the energies of the singlet and one of the triplet states varies quadratically with the strain, whereas two of the states of the triplet vary linearly with the strain. Keyes[11] pointed out that the quadratic dependence on strain of the singlet-state energy implied that elastic scattering of phonons by the electrons should occur. Keyes found that the scattering of phonons by electrons in the singlet state was proportional to ω^4 for frequencies $\omega \ll 4\Delta/h$.

There is a rapid cutoff of the scattering when the phonon wavelength is less than the donor-state radius. This is important for thermal conductivity but is unimportant for the ultrasonic wavelengths of interest here. This theory gave the first good explanation of the scattering of thermal phonons in n-type Ge, as measured by thermal conductivity.[15] When applied to the case of 9 GHz ultrasound, however, the predicted scattering is much less than the observed values in magnitude. Furthermore, the Keyes process cannot explain the various temperature dependences that we observe, since it would predict maximum attenuation to occur at $T=0$ for all species of donors. The modification of Keyes's theory suggested by Griffin and Carruthers[16] is not important for the phonon frequencies in these experiments.

In seeking another theory of phonon scattering, we return to Price's result[12] (Fig. 3). Since the singlet state considered by Keyes could not produce sufficient attenuation, we focus on the triplet states. One of these has an energy variation like the singlet [proportional to (strain)^2], but of opposite sign. When the ultrasonic wavelength is much greater than the interimpurity spacing, the effect of this state is to cancel that of the singlet state, and, in any case, will be as ineffectual as the singlet. The two remaining energy levels of the triplet vary linearly with the strain. To first order, these states cannot scatter phonons; this follows classically from the fact that there is no average energy perturbation due to these states if there are many impurity atoms per wavelength. Quantum mechanically, this perturbation is proportional to a singlecreation and annihilation operator, which cannot produce transitions that conserve energy, in first-order perturbation theory. Scattering by these states can occur only by second-order processes. In classical terms, their populations tend to relax toward a Boltzmann distribution between the linearly split states. This causes an out-of-phase

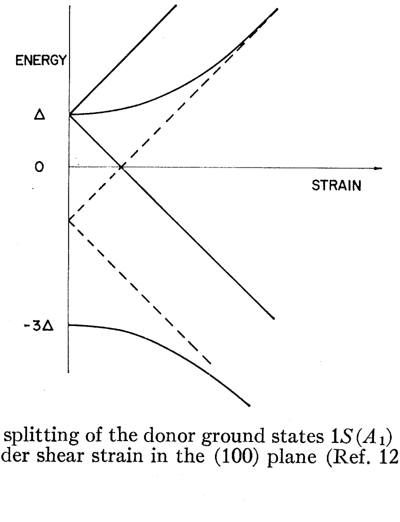

FIG. 3. The splitting of the donor ground states $1S(A_1)$ and $1S(T)$ under shear strain in the (100) plane (Ref. 12).

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[14] J. H. Reuszer and P. Fisher, Phys. Rev. **135**, A1125 (1964).

[15] J. F. Goff and N. Pearlman, Phys. Rev. **140**, A2151 (1965).

[16] A. Griffin and P. Carruthers, Phys. Rev. **131**, 1976 (1963).

TABLE I. Relaxation times of triplet states of donors.

Donors in Ge	4Δ (meV)	τ (sec) From ultrasonic attenuation	τ (sec) Optical-absorption linewidths	τ (sec) Theoretical
Sb	0.32 (Ref. 14)	2×10^{-11} (10°K)	$\gtrsim 10^{-11}$ (4°K)[a]	7×10^{-11} (4°K) (Ref. 16) 3×10^{-11} (7°K) (Ref. 24) 4×10^{-12} (10°K)[b]
P	2.83 (Ref. 14)	4×10^{-11} (20°K)	$\gtrsim 0.9\times10^{-11}$ (12°K)[c]	8×10^{-11} (12°K)[b]
As	4.23 (Ref. 14)	4×10^{-11} (20°K)	$\gtrsim 4\times10^{-12}$ (12°K) (Ref. 14)	8×10^{-10} (0°K) (Ref. 16) 2×10^{-10} (7°K) (Ref. 22) 2×10^{-10} (20°K)[b]
Donors in Si	6Δ (meV)			
P	12 (Ref. 27)	1×10^{-12} (80°K)	$\gtrsim 10^{-12}$ (80°K) (Ref. 27)	
Li	−1.6 (Ref. 29)	$\approx 3\times10^{-11}$	$\gtrsim 6\times10^{-12}$ (4°K) (Ref. 29)	

[a] May be resolution limited (see Refs. 22 and 23).

[b] N. Mikoshiba and K. Suzuki (unpublished); see Fig. 4 of this paper.

[c] May be resolution limited (see Ref. 14).

energy change that is second order in the strain, which produces attenuation. A calculation of the attenuation by such a relaxation process has been given by us[17] and independently by Suzuki and Mikoshiba.[18] P. C. Kwok[19] has given a quantum-mechanical treatment which reduces to this result in the appropriate limits. For completeness we present a derivation here.

The relaxation attenuation of the energy is given by[6]

$$\alpha = (\Delta c/cv)\omega^2\tau/(1+\omega^2\tau^2)\,, \tag{2}$$

where Δc is the equilibrium change in the elastic constant due to the relaxation process, whose relaxation time is τ. We calculate Δc by a method like that of Keyes.[20]

According to Price[12] the linearly split states of the triplet have the same energy changes as the conduction bands, $\Delta E = \pm 2\Xi_u\epsilon/3$, where ϵ is the tensor shear strain of the ultrasonic wave. The populations of electrons in these states relax toward a Boltzmann distribution in which the ratio of populations in the raised state N_+ to the lowered state N_- is $N_+/N_- = \exp(-4\Xi_u\epsilon/3kT)$. The number of electrons which relax from the upper to the lower state is half the population difference $N_- - N_+ = 4N_t(T)\Xi_u\epsilon/9kT$. Here $N_t(T)$ is the temperature-dependent population of the triplet states, and it is assumed that $4\Xi_u\epsilon \ll 9kT$. Thus the energy decrease due to relaxation is $\Delta U =$ (energy change/electron) (number of electrons that relax) $= -(\frac{4}{3}\Xi_u\epsilon)[2N_t(T)\Xi_u\epsilon/9kT] = -8\Xi_u{}^2N_t(T)\epsilon^2/27kT$. The change in elastic constant Δc_{44} is found from $\Delta U = \frac{1}{2}\Delta c_{44}e^2$, where $e = 2\epsilon =$ (the "engineering" strain),[21] to be

$$\Delta c_{44} = -4\Xi_u{}^2N_t(T)/27kT\,. \tag{3}$$

If is is assumed that the temperature is so low that only the ground singlet and triplet states are occupied, one finds that

$$N_t(T) = 3N/(3+e^{4\Delta/kT})\,, \tag{4}$$

where N is the uncompensated donor concentration. Inserting (3) and (4) into (2), we get the final result for the attenuation of the energy:

$$\alpha = \frac{4\Xi_u{}^2N\omega^2\tau}{9cvkT(3+e^{4\Delta/kT})(1+\omega^2\tau^2)}\,. \tag{5}$$

Equation (5) is plotted as the dashed curves in Fig. 1. Ξ_u was taken to be 17 eV. The values[14] of $4\Delta/k$ are 3.7°K (Sb), 33°K (P), and 49°K (As). It is the ratios of temperature to these splittings that determine the populations of the triplet state and cause the strikingly different temperature dependences. The theoretical curves were obtained by fitting the experimental data to Eq. (5) at a temperature at which the attenuation was sizable. In effect, this means finding a value of τ to give the best fit.

The most accurate method of finding τ, however, is to compare the attenuation at two different frequencies, but at the same temperature and with the same sample, if possible. Then the ratio of the attenuations is

$$\alpha(\omega_1)/\alpha(\omega_2) = N_1\omega_1{}^2(1+\omega_2{}^2\tau^2)/N_2\omega_2{}^2(1+\omega_1{}^2\tau^2)\,.$$

Finding τ using this ratio weakens the effects of material parameters which may not be accurately known. Using the data of Figs. 1 and 2 we find the relaxation times of Sb, $\tau \approx 2\times10^{-11}$ sec at 10°K; of P, $\tau \approx 4\times10^{-11}$ sec at 20°K; of As, $\tau \approx 4\times10^{-11}$ sec at 20°K. These values are listed in Table I.

To confirm this interpretation of the attenuation, it would be desirable to have independent measurements of the relaxation times of the triplet states. The only data of this kind seem to be the linewidths of the infrared absorptions by electrons in the triplet states.

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[17] M. Pomerantz, Report No. 6, Contract No. DA 36-039A MC-02280 (E), 1964 (unpublished).

[18] K. Suzuki and N. Mikoshiba, Phys. Letters **23**, 44 (1966).

[19] P. C. Kwok, Phys. Rev. **149**, 666 (1966).

[20] R. W. Keyes, IBM J. Res. Develop. **5**, 266 (1961).

[21] Cf. J. F. Nye, *Physical Properties of Crystals* (Oxford U. P., New York, 1957) for discussion of tensor versus engineering strain.

Such data have been published by Reuszer and Fisher[14,22] for As, P, and Sb and by Nisida and Horii[23] for Sb.

We must be careful, however, about the assumption that the linewidth is caused by the lifetime of the state, which we should like to compare to the relaxation time found from the ultrasonic measurements. Nisida and Horii[23] have studied the concentration dependence of the linewidths of Sb. They found that even for concentrations as low as $\approx 10^{15}$ Sb/cc there may already be a concentration-dependent linewidth. In addition, the lines resulting from excitation from the $1S\,(A_1)$ singlet and $1S(T_1)$ triplet to various excited p states were found to have different widths. Also, the transitions terminating in the same p state had different widths. These facts suggest that the broadening involves strains caused by the Sb atoms themselves. We hope to discuss this in detail in a subsequent paper, but for the present it will be assumed that the minimum linewidth represents the upper limit of the intrinsic lifetime of isolated Sb donors.

The minimum linewidth is observed for the lowest concentration and the $1S(T_1) \rightarrow 2p_0$ transition. The half-width at half-maximum is $\Delta E \approx 0.06$ meV and may be instrument limited. Thus, the lifetime broadening of the triplet state, $\tau \gtrsim h/\Delta E \approx 10^{-11}$ sec for Sb. Similarly, the minimum absorption linewidth[14,22] for As is $\Delta E \approx 0.14$ meV and for P, $\Delta E \approx 0.07$ meV. These correspond to lifetimes $\tau(\text{As}) \gtrsim 4\times10^{-12}$ and $\tau\,(P) \gtrsim 9\times10^{-12}$, where the latter may be resolution limited. In Table I these values are collected with those derived from the ultrasonic measurements. It is seen that the ultrasonic values are consistent with the optical ones. Furthermore, the ultrasonic method can establish the value of τ in cases where the optical measurement is instrument limited.

There have been several theoretical calculations of the linewidths, or lifetimes, of the triplet states. Perhaps the first of these was by Twose[24] who calculated $\Delta E = 3\times10^{-3}$ meV for As and $\Delta E = 2\times10^{-2}$ meV for Sb at 7°K. These correspond to $\tau = 2\times10^{-10}$ sec for As and $\tau = 3\times10^{-11}$ sec for Sb. Griffin and Carruthers[16] calculated the lifetime due to interaction with thermal phonons and found for As, $\tau \approx 8\times10^{-10}$ sec and for Sb, $\tau \approx 1\times10^{-10}$ sec, at $T = 0°\text{K}$. They also point out that the calculated relaxation times depend strongly on the values of the donor Bohr radii. If the temperature dependence of τ is included, these values become smaller and approach those of Twose. Kwok's[19] theory yields an expression for τ, which is the same as Griffin and Carruthers's. Suzuki and Mikoshiba[18] also give an expression for τ which is based on phonon relaxation, but which gives somewhat shorter relaxation times, viz., for As, $\tau \approx 2\times10^{-10}$ sec and for Sb, $\tau \approx 2\times10^{11}$ sec, at 0°K. By courtesy of Dr. Mikoshiba and Dr. Suzuki we reproduce their unpublished calculations of τ as a function of T in Fig. 4. For Sb the theoretical values bracket the experimental one within about an order of magnitude. For P the agreement is good. For As the disagreement is somewhat more than an order of magnitude. It should be noted that for As two different concentrations of impurities were used at the two frequencies. This may introduce some error because of interaction of the impurities.

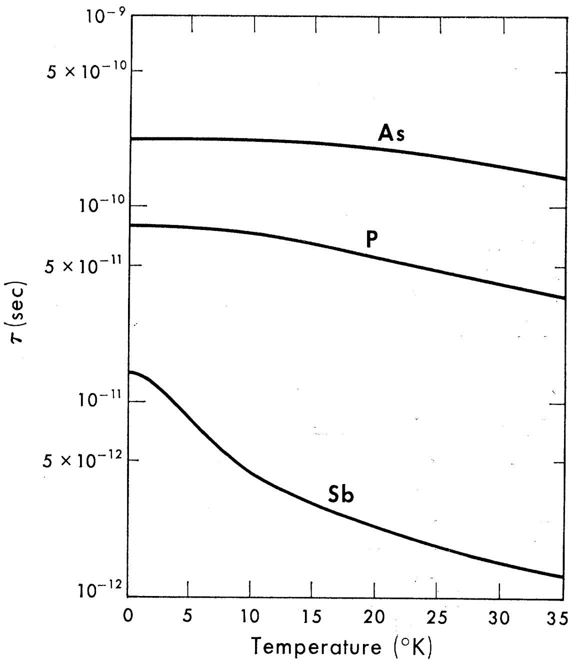

FIG. 4. Temperature dependence of the relaxation times of the triplet states of Sb, P, and As donors in Ge (unpublished calculations of Dr. N. Mikoshiba and Dr. K. Suzuki).

It is perhaps significant that if τ is derived from the 9-GHz data and Eq. (5) using values of donor density found from room-temperature resistivity that the values come out to be much too short. One gets $\tau \approx 2\times10^{-12}$ sec, which is inconsistent with some of the optical data and the theories. A possible explanation of this is that many of the donors are in strained sites. A local strain large enough to split the states by an amount $\gtrsim kT \approx 4\Delta$ would cause the upper states to be thermally depopulated, reduce the attenuation, and give too short τ. This would require a strain of the order of $\epsilon \gtrsim 4\Delta/\Xi \approx 10^{-4}$ for As and $\approx 10^{-5}$ for Sb. Local strains of $\approx 10^{-5}$ have been observed[25] for As in Ge, and significant effects of strain on Sb in Ge have been suggested.[26] Particularly in the case of Sb, which has a small 4Δ, relatively small strains may reduce the attenuation produced by a sizable fraction of the donors. Also, the values of τ for P and As are determined

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[22] J. H. Reuszer and P. Fisher, Phys. Rev. **165**, 909 (1968).

[23] Y. Nisida and K. Horii, J. Phys. Soc. Japan **26**, 388 (1969).

[24] W. D. Twose, quoted by H. Fritzsche, Phys. Rev. **120**, 1120 (1960).

[25] D. K. Wilson, Phys. Rev. **134**, A265 (1964).

[26] R. E. Pontinen and T. M. Sanders, Jr., Phys. Rev. **152**, 850 (1966).

from attenuation at about 20°K. At this temperature there is some thermal excitation out of the ground states which would give erroneously short values of τ from Eq. (5). This is why it is preferable to obtain τ from the ratio of attenuation at two frequencies in the same sample at the same temperature.

The experimental fact that only waves whose elastic constant contains c_{44} are strongly attenuated also follows from this theory. Only shear strains that lift the degeneracy of the (111) valleys cause splittings of the donor states.[12] The elastic constant of such a wave contains c_{44}.

V. *n*-TYPE Si

The explanation of the attenuation due to donors in Ge can be extended to other materials; in particular we have made measurements in *n*-type Si. The major differences between *n*-type Ge and *n*-type Si are that the conduction bands of Ge have four minima in the $\langle 111\rangle$ directions, whereas the conduction bands of Si have six minima in the $\langle 100\rangle$ directions in k space. Thus, donors in Si have different symmetry and degeneracy from donors in Ge. Optical-absorption studies[27] of donors in Si have shown that the sixfold-degenerate-donor ground state is split into singlet (A_1), doublet (E), and triplet (T_1) states for P, As, Sb, and Bi donors. Because of the $\langle 100\rangle$ valley symmetry, one expects[28] that strain waves involving the elastic constants c_{11} or c_{12} would further split the degeneracies and lead to attenuation of the waves. (This is unlike Ge in which the elastic constant c_{44} is connected with attenuation.) A quantitative difference from Ge arises from the magnitude of the splittings between the singlet and the $1S(E)$ and $1S(T_1)$ states. In Si this splitting is about[27] 10 meV for P, As, and Sb donors. Thus, the degenerate states become occupied at temperatures of the order of 100°K for these substitutional donors in Si.

A formula for the attenuation by donors in Si can be derived, analogous to that derived in Sec. IV for Ge. We find for the slow shear wave in the [110] direction,

$$\alpha=\frac{N\Xi_u^2}{kTcv(e^{6\Delta/kT}+5)}\frac{\omega^2\tau}{1+\omega^2\tau^2}, \tag{6}$$

where N is the concentration of uncompensated neutral donors, 6Δ is the energy separation between the $1S(A_1)$ and the $1S(E)$ and $1S(T_1)$ states, the latter two being taken to be at the same energy, and Ξ_u is the shear deformation potential constant of Si$\approx$11 eV. Assuming τ is independent of T, the attenuation is a maximum at a temperature $T_m=6\Delta/1.8k$. For P donors in Si, $T_m=78$°K.

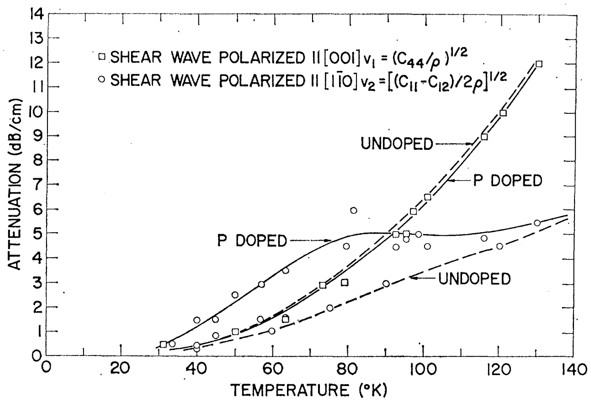

FIG. 5. Temperature dependence of the attenuation of the shear waves propagating in the [110] direction of pure and P-doped Si. The ultrasonic frequency is 9 GHz and the P concentration is 6×10^{15}/cc.

Figure 5 shows our measurement of the attenuation of 9-GHz shear waves in the [110] direction of Si doped with P to a concentration of $6\times10^{15}/\text{cm}^3$. It was found that there is an excess attenuation for the slow shear wave whose velocity is given by $v=[c_{11}-c_{12}/2\rho]^{1/2}$. This attenuation has a maximum value at about 80°K, which is in reasonable agreement with the expected temperature dependence. The shear wave whose velocity $v=(c_{44}/\rho)^{1/2}$ is unaffected by the donors.

The attenuation versus T was measured at 3 GHz in a more heavily doped sample containing $\approx 7\times10^{16}$ P/cc. The results (Fig. 6) show an excess attenuation for the slow shear wave which peaks at 80°K, as for the 9 GHz waves. The fact that the excess attenuation at the lower frequency is approximately the same magnitude as at 9 GHz despite about a tenfold increase in concentration, indicates a strong dependence on frequency. This suggests that we are in the $\omega\tau\ll1$ region, in which $\alpha\propto\omega^2\tau$. We must then calculate τ from Eq. (6). The results are $\tau=1.6\times10^{-12}$ sec, using the 9-GHz data and $\tau=1.2\times10^{-12}$ sec using the 3-GHz data. Within experimental error we consider these to be equal.

The optical absorption from the $1S(T_1)$ state to excited p states has been observed[27] and we can compare these linewidths with the relaxation time. For P in Si, the linewidth of the $1S(T_1)\rightarrow 2p_0$ transition was $\approx$0.6 meV, which corresponds to a lifetime of $\gtrsim10^{-12}$ sec. We find therefore that the use of Eq. (6) with N determined by a transport measurement, gives good agreement between the optical and acoustical results (cf. Table I). This was not the case in Ge, where only the ratio of attenuations at two frequencies gave consistent results. This is reasonable because strains may be reducing donor scattering in Ge. But in order for strains to have an effect in Si, their magnitude must be $\epsilon\gtrsim kT/\Xi\approx10^{-3}$, because $T\approx100$°K when the attenuation is large. Apparently such large local strains are not present, and all the donors are effective scat-

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[27] R. L. Aggarwal, Solid State Commun. 2, 163 (1964); R. L. Aggarwal and A. K. Ramdas, Phys. Rev. **140**, A1246 (1965).

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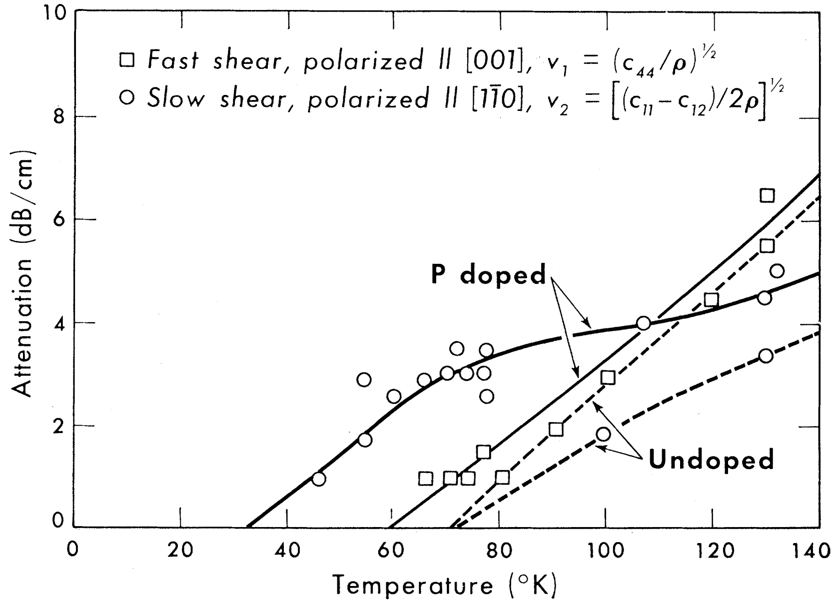

FIG. 6. Temperature dependence of the attenuation of the shear waves propagating in the [110] direction of pure and P-doped Si. The ultrasonic frequency is 3 GHz and the P concentration is 7×10^{16}/cc.

terers. There may be thermal excitation out of the ground states, so that the ultrasonically determined relaxation time given in Table I is probably too small. Thus, τ is probably $>10^{-12}$ sec, but the condition $\omega\tau\ll1$ says that $\tau\ll3\times10^{-11}$ sec. This suggests that a reasonable order of magnitude of τ is 5×10^{-12} sec.

An interesting case is presented by Li donors in Si. Aggarwal *et al.*[29] have shown that Li can form two donor structures, a Li-O complex if oxygen is present, or isolated Li atoms. In the Li-O complex, the energies of the levels follow the same order as the other donors in Si and Ge, i.e., the singlet is lowest. In the case of the isolated Li, however, they find that the order is inverted, so that the degenerate states are lowest in energy. This means that even at the lowest temperatures there is more than one occupied state. Under the influence of the ultrasonic strain wave the relative energies of the occupied states may be changed, and attenuation should result, even at low temperature. We have verified this prediction in a [110]-oriented Si bar doped with 1×10^{16} Li/cc. The Si was prepared such that the Li was in the isolated donor form, i.e., oxygen-free Si. The shear wave with velocity $v=(c_{44}/\rho)^{1/2}$ seemed unaffected by the doping, but the shear wave whose velocity$=[(c_{11}-c_{12})/2\rho]^{1/2}$ was not observed at any temperature, at either 9 or 3 GHz. The magnitude of the attenuation seems exceptionally large; it must be >10 dB/cm at all temperatures. In our explanation, this implies that the relaxation time is of the order $1/\omega$, $\approx3\times10^{-11}$ sec. The temperature dependences of the population and the relaxation time appear to combine such as to give high attenuation, but we do not understand this completely.

VI. SOUND-VELOCITY CHANGES DUE TO DONORS

For Ge it was found that electrons in the triplet state can produce a change in the elastic constants given by Eqs. (3) and (4), which combine to give

$$\Delta c_{44,L} = -4\Xi_u^2 N/9kT(3+e^{4\Delta/kT}) . \qquad (7)$$

The subscript L indicates that this effect arises from the triplet states whose energies vary linearly with strain. The change in elastic constant arises from population redistribution, a second-order effect. Keyes[30] has predicted a change in the elastic constants that results from the quadratic dependence of the energy of the singlet and one of the triplet states on the strain (cf. Fig. 3). The formula he derived,

$$\Delta c_{44} = \frac{-N\Xi_u^2[(4\Delta/kT)-1+e^{4\Delta/kT}]}{18\Delta(3+e^{4\Delta/kT})}, \qquad (8)$$

actually includes the effect of all four donor ground states.[31] To separate the contribution of the linearly varying levels from the quadratically varying levels we form the ratio

$$\frac{\Delta c_{44,L}}{\Delta c_{44}} = 2\left(\frac{4\Delta}{kT}\right)\Big/\left(\frac{4\Delta}{kT}-1+e^{4\Delta/kT}\right). \qquad (9)$$

From Fig. 7, which is a plot of Eq. (9) as a function of $T/(4\Delta/k)$, it can be seen that for $kT\ll4\Delta$ the linear states contribute little to Δc_{44}. This is because of freeze out of the electrons into the singlet state. At

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[29] R. L. Aggarwal, P. Fisher, V. Mourzine, and A. K. Ramdas, Phys. Rev. **138**, A882 (1965).

[30] R. W. Keyes, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1968), Vol. 20, p. 37; and Ref. 20.

[31] R. W. Keyes (private communication).

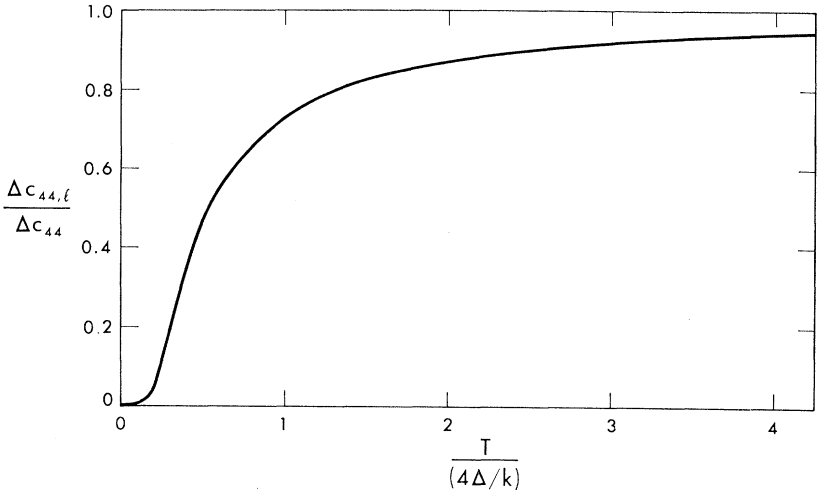

FIG. 7. Temperature dependence of the ratio of the change in the elastic constant of Ge due to the $1S(T_1)$ levels that vary linearly with the strain to the total change in elastic constants due to electrons in the donor $1S(A_1)$ and $1S(T_1)$ states.

higher temperatures, $kT \approx 4\Delta$, the quadratic effect is reduced. This results from the occupancy of the triplet state which varies quadratically with strain, but in the sense opposite to the singlet. Of course, the "linear" effect becomes larger as the triplet states that vary linearly with strain are thermally populated. In the limit of $kT \gg 4\Delta$ the linear effect seems to be the entire effect. There may be a numerical error, however, because it is not reasonable that the quadratic states contribute nothing. It is more likely that the linear and quadratic states make comparable contributions to Δc_{44} at high temperatures.

The order of magnitude of the change of the elastic constants by electrons bound to donors has been estimated by Keyes[30] to be, for Sb donors, $(\Delta c_{44}/c_{44})_{T=0} = N\Xi_u^2/18c_{44}\Delta = -N/3.5\times10^{18}$. Thus for concentrations $N \approx 3\times10^{15}$ cm^{-3} there is $\approx 0.1\%$ change in the elastic constants, which is quite within the state of the art in ultrasonic velocity measurements. Hall[32] has measured the decrease in the elastic constants caused by 3.5×10^{15} Sb cm^{-3} and finds good agreement with Keyes's theory Eq. (8).

VII. SUMMARY AND DISCUSSION

We have described the observation of attenuation of microwave phonons by donors in Ge and Si. The mechanism we proposed involves the relaxation of bound electrons between levels whose relative energies are changed by the ultrasonic strain. Thus, this effect enables one to investigate (a) the relaxation times of the energy levels, for which the frequency dependence is measured, (b) the energy separation of the relevant energy levels, which is studied by the temperature dependence of attenuation, and (c) the symmetry of the relevent states, which is manifested in the polarization dependence.

As a continuation of this work on donors, we have observed the attenuation due to bound holes on acceptors in Ge and Si. The effects and their interpretation are more complicated, and we hope to present these in another paper.

We may remark that attenuation by bound carriers may be important in other experiments. For example, in the amplification[33] of microwave phonons in Ge, it is helpful to use As-doped Ge because in operating at 4°K there is negligible attenuation by the bound electrons. Application of an electric field impact-ionizes the carriers, which may produce amplification. If Sb-doped Ge is used, the interpretation is not as clear because impact ionization frees the bound electrons, thereby reducing the attenuation; this may be mistaken for amplification.

In the observation of ultrasonic spin-resonance absorption by donors[34,35] it is imperative to avoid using Sb-doped Ge, because the wave that interacts with the spin system will be strongly absorbed.

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