of 2.20 ± 0.02 ev with a half-width of a few kT. This value is a few hundredths of an electron volt lower than the peak obtained from the van Roosbroeck-Shockley theory[2] using the calculated α's (derived from the Macfarlane-Roberts analysis), but agrees well with the peak obtained using the above-discussed additional low-energy absorption. It is interesting to note that a comparison of the high-energy side of the spectral curve of electroluminous emittance to the van Roosbroeck-Shockley theory indicates a photon travel through GaP of about 10^{-2} cm. This is in rather good agreement with the value obtained from the photocurrent vs $h\nu$ analysis. Some of the additional low-$h\nu$ emission is most likely due to defect sites mentioned above. These and self-absorption cause the peak to shift somewhat to lower energies.

We conclude that most of the electroluminescent phenomena on hand are quite distinct from those originating from recombinations via defect states as reported previously.[1,12] In all the latter cases the photon distribution peaks at energies lower than the energy gap value obtained from free carrier recombination electroluminescence reported in this Letter, or from the analysis of other optical data. Also in all defect center recombination cases a linear dependence of the light on current has been found. The agreement between the above-discussed characteristics of electroluminescence, optical absorption, and photoelectric response leads us to identify the electroluminescent phenomenon as one primarily due to band-to-band bimolecular transitions.

We have also seen bimolecular recombination kinetics for radiative transitions of carriers injected across a rectifying junction in indium phosphide. Braunstein[5] reported the presence of recombination radiation in InP at an energy close to the band gap. We have obtained the spectral distribution of this radiation. It is shown in Fig. 2. The position of the peak at 1.25 ev is in good agreement with the band gap values reported in the literature.[13]

The authors wish to express thanks to R. Braunstein, A. R. Moore, and J. I. Pankove for helpful discussions.

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ELECTRON SPIN RESONANCE EXPERIMENTS ON SHALLOW DONORS IN GERMANIUM

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Electron spin resonances on shallow donors in silicon have been studied by several authors.[1-3] In germanium there are various factors which make the observation of electron spin resonance signals more difficult and, so far, no resonances have been reported on shallow impurity states. The recent conflicting experimental results pertaining to the donor ground state in germanium[4,5] led us to reinvestigate the electron spin resonance behavior in this material. In the present Letter we wish to report on the observation of electron spin resonances from both bound and nonlocalized electrons in germanium. The results indicate that the ground state of the arsenic and phosphorus donors in germanium is a singlet.

The experiments were performed at temper-

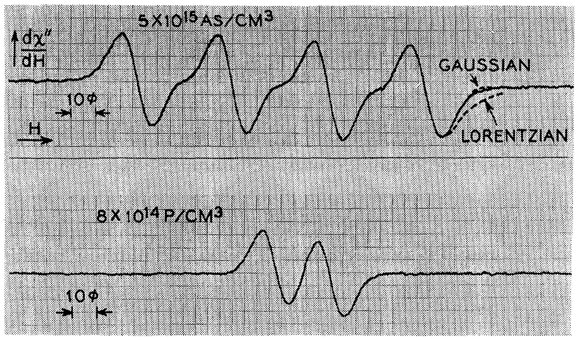

FIG. 1. Electron spin resonance signal from arsenic and phosphorus donors in germanium with the magnetic field H parallel to the [100] direction. $T \simeq 1.3$°K; $\nu_e \simeq 9000$ Mc/sec.

atures between 1.3°K and 4°K and microwave frequencies of ~9000 Mc/sec and ~24 000 Mc/sec. The details of the spectrometer have been described elsewhere.[6]

At low donor concentrations the electrons are localized on the impurity and a resolved hyperfine interaction with the donor nucleus is observed. This is illustrated for arsenic ($I=\frac{3}{2}$) and phosphorus ($I=\frac{1}{2}$) doped germanium in Fig. 1. The experimental results on the line width ΔH (full width between inflection points of $d\chi''/dH$), hyperfine splitting, and g values are summarized in Table I. The experiments on the arsenic-doped sample were repeated at 24 000 Mc/sec. The g value, ΔH (with H parallel to [100]), and hf splitting were found to be the same as at the lower frequency. For comparison purposes the data on silicon[1,3] are also listed in Table I.

The g shift in germanium is about two orders of magnitude larger than in silicon. It is proportional to $\lambda/\Delta E$, where λ is the spin-orbit coupling which in the valence band of germanium is an order of magnitude larger than in silicon and ΔE is the energy separation of the nearest bands that are admixed. The large observed g shift may have contributed to the fact that these lines have previously been missed.

The line widths quoted in Table I were obtained with H parallel to the [100] direction. When H deviates from this direction an appreciable line broadening occurs. This broadening together with the necessary small donor concentration in germanium makes the observation of the lines more difficult than in silicon. The broadening may arise, either from the anisotropic part of the hf interaction with the germanium nuclei or from a spread in g values due to a local perturbation of the donor wave function[7] (e.g., due to strains or overlaps). The observed Gaussian line shape is consistent with either picture. Experiments are under way to shed light on this question.

The magnitude of the hf splitting is about a factor of two smaller than in silicon. By a simple extrapolation of the theory of shallow donors in silicon due to Kohn and Luttinger,[8,9] one expects the hf splitting in germanium to be approximately an order of magnitude smaller than in silicon. This discrepancy with the experimental results is consistent with the large observed line width and indicates that the peaking of the conduction band wave functions at the nuclei is about

Table I. Summary of electron spin resonance data on phosphorus- and arsenic-doped germanium and silicon.[a,b] Because of different passage conditions[b] the line width in silicon has to be multiplied by 0.85 before comparing it to germanium.

Donor	Donor concentration (cm^{-3})	g value	Line width ΔH (oersteds)	Total hf splitting (oersteds)	$\lvert\psi(0)\rvert^2$ (cm^{-3})
		Germanium			
Phosphorus	8×10^{14}	1.5631 ± 0.0003	10	21	0.21×10^{24}
Arsenic	5×10^{15}	1.5701 ± 0.0003	11	107	0.87×10^{24}
		Silicon			
Phosphorus	1.5×10^{16}	1.99850	2.8	42	0.43×10^{24}
Arsenic	1.8×10^{16}	1.99837	3.2	212	1.73×10^{24}

[a] See reference 1.
[b] See reference 3.

a factor of six larger in germanium than in silicon. However, in deciding whether the singlet or the triplet is the lowest state only the presence of an appreciable isotropic hf interaction is important. Kohn and Luttinger[8,9] have shown that the ground-state wave function can be made up of a linear combination of four wave functions corresponding to the four minima of the conduction band. For three of these combinations (which form the degenerate triplet state) the value of the wave function at the origin is zero, and therefore cannot give rise to the observed isotropic hyperfine interaction. The singlet state is formed from a linear combination that has a finite value of $|\psi(0)|^2$ and should give rise to a hf splitting. The experimental observation of a splitting indicates therefore that the ground state is the singlet. The absolute amplitude of the signal and its variation with temperature excludes the possibility that one is observing an excited state.

At high donor concentrations[10] the electron is no longer localized on a particular impurity but moves throughout the crystal giving rise to a conduction process ("impurity band conduction") even at the lowest temperatures. Under these conditions the hyperfine interactions are averaged out and a single resonance line is observed.[11] The line width for such nonlocalized electrons in germanium is found to be anisotropic as illustrated in Fig. 2 which shows the results on a phosphorus-doped sample (10^{17} P/cm^3, $T = 1.3$°K, $\nu_e \simeq 9000$ Mc/sec). The width presumably arises from a spread in electronic g values which, in contrast to silicon,[11] are incompletely averaged out by motional narrowing.[12] An increase in temperature from 1.3°K to 4°K decreased the line width in the above phosphorus sample by ~10%. Similarly, an increase in the concentration from 3×10^{16} P/cm^3 to 10^{17} P/cm^3 decreased the line width in the [100] direction from 6 oersteds to 4 oersteds. These results and the observed Lorentzian line shape support the picture of a motionally narrowed line.[12]

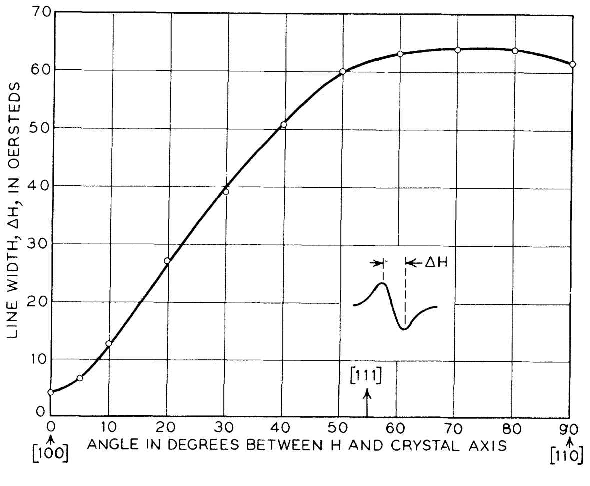

FIG. 2. Line width as a function of the orientation of the magnetic field with respect to the crystalline axes. $T \simeq 1.3$°K; $\nu_e \simeq 9000$ Mc/sec; 10^{17} P/cm^3. In this impurity concentration range one observes a single resonance line due to nonlocalized electrons.

The electronic g value of the nonlocalized electrons was found to be isotropic and approximately equal to the g value of the bound electrons (e.g., for 10^{17} P/cm^3, $g = 1.5636 \pm 0.0003$; and for 10^{17} As/cm^3, $g = 1.5698 \pm 0.0003$). This indicates that in this concentration of "impurity banding" the electron spends most of its time on the impurity.

Antimony-doped germanium was investigated in the concentration range between 10^{15} Sb/cm^3 and 3×10^{16} Sb/cm^3. The line shape was found to be extremely asymmetric and the g value varied between ~1.6 with H parallel to the [100] direction and 1.9 with H parallel to the [110] direction. This striking difference in behavior indicates that either the triplet-singlet levels overlap or that perhaps the triplet is lower in antimony. Strain experiments are in progress which should decide on this question.

We profited greatly from discussion with many members of the Bell Telephone Laboratories. In particular we wish to acknowledge the stimulating discussions with W. Kohn, P. W. Anderson, and G. Weinreich. We also wish to thank G. Bemski and J. Eisinger for their help in the 24 000-Mc/sec experiment.

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[7] This would cause a mixing of the singlet and triplet states. However, in the [100] direction the four conduction band minima are equivalent and the mixing would not cause a broadening. This picture is consistent with the result that the narrowest line is ob-

served in the [100] direction.

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[10] In silicon this occurs at concentrations of the order of 10^{17}-10^{18} donors/cm^3. Because of the larger impurity Bohr radii in germanium, the corresponding concentrations are lower by between one and two orders of magnitude.

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ABSORPTION OF COMPRESSIONAL WAVES IN SOLIDS FROM 100 TO 1000 Mc/sec

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We have determined the absorption of compressional waves in crystal quartz [X-direction], fused silica, germanium [100], and silicon [111]: the crystallographic directions specify the direction of propagation. Measurements were made by the "pulse technique" using guided waves in cylindrical specimens.[1-3] The dependence of the amplitude absorption coefficient on frequency is shown in Figs. 1-4.

In contrast to the findings of Granato and Truell and their co-workers[4-7] for germanium, we observed little difference between the absorption values for five crystals of silicon from different sources. These had dislocation densities—revealed by etch pits—from a few hundred to over 10^4 per cm^2. Two specimens were n-type with average resistivities of 0.1 and 14 ohm-cm, and three were p-type with resistivities of 3.20 and 30 ohm-cm. The axis of each cylinder was within 3° of the [111] direction. The absorption values in all five specimens agreed to within ± 5 %.

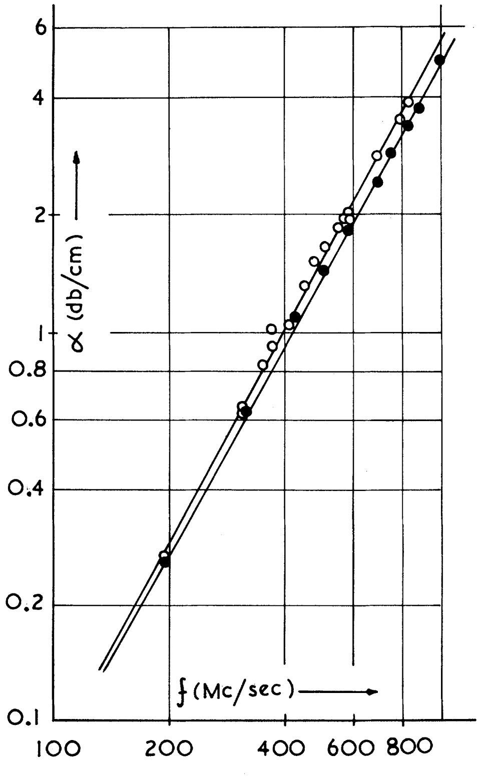

FIG. 1. Log(absorption coefficient) versus log(frequency) in crystal quartz. Propagation is along the X-axis. ○ = 20°C; ● = -77°C. At 20°C, α is proportional to $f^{1.82}$

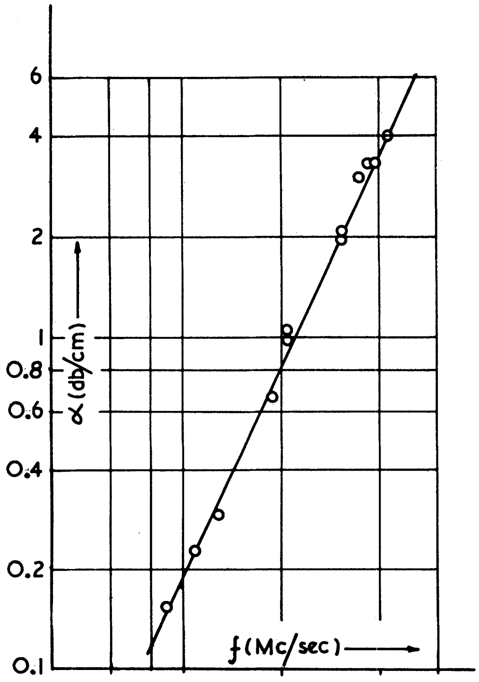

FIG. 2. Log(absorption coefficient) versus log(frequency) in fused silica (Thermal Syndicate, O.G. grade) at 18°C: α is proportional to $f^{2.12}$.

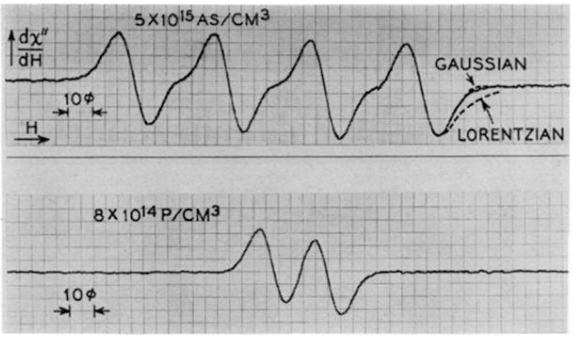

FIG. 1. Electron spin resonance signal from arsenic and phosphorus donors in germanium with the magnetic field $\boldsymbol{H}$ parallel to the [100] direction. $T \simeq 1.3$°K; $\nu_e \simeq 9000$ Mc/sec.