In all the samples a small stress dependence of the g value was observed. Its value for the boron-doped samples was found to be $\Delta g_\perp/\Delta T = 7\times10^{-5}$ cm^2/kg. Experiments were also performed with the stress applied along the [111] and [110] directions. The g values for these stress directions differed by a few percent from the above quoted values. In order to evaluate the significance of these differences, experiments are presently being carried out to extrapolate the g values to zero stress. For free holes one can show theoretically that $g_\parallel = 2\kappa$, where κ is the additional valence parameter introduced by Luttinger,[2] and $g_\perp/g_\parallel = 2$. The best agreement with this ratio would be expected for acceptors with the smallest binding energy (boron), a fact which is confirmed experimentally.

In the course of measuring the g anisotropy the angle θ between the microwave field $\vec{H}_1$ and static magnetic field $\vec{H}_0$ was varied. (The microwave magnetic field $\vec{H}_1$ was parallel to the stress axis $\vec{T}$). The transition probability between two pure $M_J = \pm 1/2$ states should be proportional to $\sin^2\theta$. By measuring the amplitude of the resonance signal we found a large deviation from the $\sin^2\theta$ dependence which indicates an admixture of the $M_J = \pm 3/2$ state.

We would like to express our appreciation to W. Kohn whose remarks stimulated these experiments and to Y. Yafet and M. Lax for helpful discussions.

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NEW ELECTRON SPIN RESONANCE SPECTRUM IN ANTIMONY-DOPED GERMANIUM*

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We report here the observation in the liquid helium temperature range of an apparently new electron spin resonance spectrum in antimony-doped germanium. The spectrum consists of four lines each with an anisotropic g factor. The four g tensors are ellipsoids of revolution with the symmetry axes pointing in [111] directions. The principal g values are in agreement with theoretical[1] and experimental[2] values for electrons in the four minima of the conduction band of germanium. Measurement of the temperature dependence of the intensity of the resonances and the independence of the intensity of the presence of far-infrared radiation indicates, however, that the spectrum is not due to electrons excited across a finite gap into the conduction band. Among the models which might fit the experimental behavior are electrons in an impurity band or a combination of an antimony donor and another point defect in nearest neighbor positions. No similar spectrum has been observed in arsenic-doped germanium. The resonance associated with electrons bound to the donors (previously reported by Feher, Wilson, and Gere[3]) is also observed in the same samples. We will refer to this resonance as the donor electron resonance, and to the four-line spectrum reported here as the new resonances.

The measurements were performed on five antimony-doped samples ranging in nominal impurity concentration from 7×10^{15} to 5×10^{16} donors per cm^3 (0.4 to 0.06 ohm-cm room temperature resistivity[4]). The samples were oriented by reflection of light from etch pits[5] and were placed in a silver-plated brass reflection cavity in a two-bolometer bridge X-band spectrometer. The samples were mounted so that the microwave magnetic field pointed in the $[1\bar{1}0]$ direction and the static magnetic field could be rotated in the $(1\bar{1}0)$ plane. The cavity was located in a helium cryostat which includes provisions for temperature stabilized operation at temperatures above 4.2°K. The present measurements were made in the range from 1.2°K to 5.0°K.

For electrons with a spheroidal g tensor, one has

$$g^2 = g_\parallel^{\,2}\cos^2\phi + g_\perp^{\,2}\sin^2\phi, \qquad (1)$$

where $g_\parallel$ and $g_\perp$ are the principal g values, parallel and perpendicular to the symmetry axis, respectively, and ϕ is the angle between $\vec{H}_0$ and the symmetry axis. For a general orientation of $\vec{H}_0$ four resonances will appear, but for $\vec{H}_0$ in

a (110) plane and the symmetry axes in [111] directions two of the symmetry axes lie in the plane and the other two are out of the plane but make equal angles with $\vec{H}_0$. Thus three resonances should be observed. We have determined the parameters $g_{\parallel}$ and $g_{\perp}$ by plotting g^2 versus $\sin^2\phi$ for the two spheroids whose symmetry axes lie in the plane of rotation. The data fit a straight line in such a plot and yield the values:

$$g_{\perp} = 1.922 \pm 0.007, \quad g_{\parallel} = 0.820 \pm 0.008. \qquad (2)$$

These numbers are consistent with the conduction electron values $g_{\perp} = 1.92 \pm 0.05$ and $g_{\parallel} = 0.87 \pm 0.05$ reported by Wilson and Feher[2] by observing the g anisotropy produced in the spectrum of electrons bound to arsenic donors in germanium when the crystal is strained. The values are also consistent with the theoretical predictions of Roth and Lax[1] for conduction electrons, $g_{\perp} \cong 2.04 \pm 0.04$ and $g_{\parallel} \cong 0.9$. The g values predicted by Eq. (1) using the parameters of Eq. (2) are plotted versus orientation of $\vec{H}_0$ in Fig. 1.

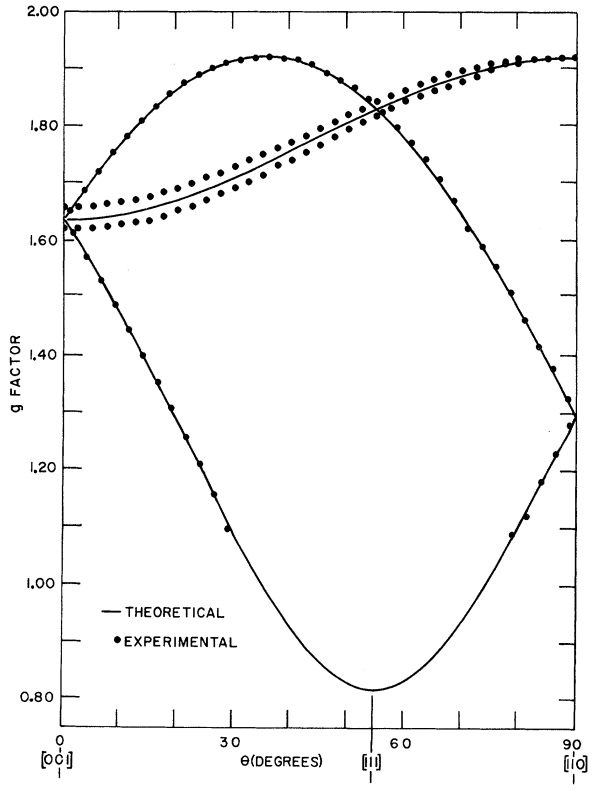

FIG. 1. g factor of electrons in antimony-doped germanium. The theoretical curve is drawn for $\vec{H}_0$ in the (1$\bar{1}$0) plane. The sample is misoriented approximately 1.5°. The donor resonance is not shown. θ is the angle between $\vec{H}_0$ and the [001] direction.

On the same plot are shown experimental points. There appears to be good agreement, and the splitting of the resonances due to the spheroids whose symmetry axes are out of the (1$\bar{1}$0) plane can be explained by a sample misorientation of approximately 1.5°. This misorientation does not appreciably affect the parameter determination described above. The misorientation also serves to show that there are four resonances and excludes the possibility that the lines might be due to electrons in the low-lying triplet state. We find the width and shape of these resonances to be anisotropic and temperature independent in the range from 1.2°K to 5.0°K. The lines are somewhat asymmetric and have a width between inflection points varying from approximately 6 gauss near $g = 1.92$ to 17 gauss near $g = 1.1$, the lowest g value observable with our magnet. An approximate upper limit for the product T_1T_2 can be set by our inability to saturate the lines at power levels up to approximately 1.5 milliwatts, i.e., microwave magnetic fields up to 0.2 gauss. We obtain $T_1 < 5\times10^{-6}$ sec; 2×10^{-8} sec $\leq T_2 < 3\times10^{-7}$ sec.

The temperature and sample dependence of the spectrum has also been studied. The area under the absorption curves has been compared with the area under the donor electron resonance and also that produced by a DPPH sample located on another wall of the cavity. The data, which are not very precise, can be summarized as follows. For the samples studied, the number of electrons contributing to the new electron resonances is very nearly temperature independent from 1.2°K to 5.0°K. By contrast, the number of electrons contributing to the donor resonance decreases markedly as the temperature is raised.[6] The intensity of the new electron resonance in the different samples is proportional to the doping and to the intensity of the donor electron resonance. The ratio of the number of electrons contributing to the new resonances to the number contributing to the donor electron resonance at 1.2°K is 0.026 ± 0.003 for all samples studied. To obtain this last number one must evaluate the transition matrix elements for a spheroidal g tensor. An elementary calculation yields for our geometry:

$$|M|^2 = |(f|-\vec{\mu}\cdot\vec{H}_1|i)|^2 = (\tfrac{1}{2}g_{\perp}\beta H_1)^2 \qquad (3)$$

for the "in-plane" spheroids and

$$|M|^2 = (\tfrac{1}{2}g_{\perp}\beta H_1)^2\left[\frac{\sin^2\theta}{2+\sin^2\theta} + \left(\frac{g_{\parallel}}{g}\right)^2 \frac{2}{2+\sin^2\theta}\right] \qquad (4)$$

for the "out-of-plane" spheroids, where β is the Bohr magneton, θ the angle used in Fig. 1, and g^2 is given by Eq. (1). This is to be compared to $|M|^2 = (\frac{1}{2} g\beta H_1)^2$ for the isotropic case. The orientation dependence of the line intensities has been checked roughly and appears to be in agreement with Eqs. (3) and (4).

We have searched for the spectrum in germanium containing 7×10^{16} arsenic donors per cm^3. In the temperature range 1.3°K to 8°K, no such resonances were found. We have also studied less extensively arsenic-doped germanium containing 7×10^{15} and 2.8×10^{16} donors per cm^3 and failed to observe any similar resonances.

Finally we may remark that we do not yet understand the nature of the states of these electrons. The possibilities we have considered include electrons excited to the conduction band, electrons localized around a defect having axial symmetry, and electrons in an impurity band. None of these models seems to be consistent with all the data. Thermal excitation to the conduction band is inconsistent with the observed temperature independence of the number of electrons contributing to the resonance and would in any case be expected to be negligible in this temperature range. Excitation to the conduction band by infrared-induced ionization of the donors seemed to be a possibility, but we have excluded it by a series of experiments in which we used infrared filters and sources which should have caused large changes in the intensity of far-infrared radiation at the sample. No changes in the resonances were detected.

The spectrum may be produced by a combination of an antimony donor and another point defect in a nearest neighbor position. This complex could produce four resonances having the required type of anisotropy. We can cite the following arguments against this possibility. First, the resonances are very much narrower than those of the electron bound to donors (6 gauss compared with a minimum of 50 gauss). One would expect considerable hyperfine broadening for such a defect, and this could not be motionally narrowed without also varying the anisotropy. Second, the agreement between the observed g values and those of the conduction band would become fortuitous. Third, it is difficult to see why only antimony-doped samples should show such a spectrum and why complexes involving more distant neighbors are not seen. Fourth, the chances seem very remote that three percent of the donors in five modern germanium crystals would find themselves located next to a defect.

Finally, we must consider the possibility that these are mobile electrons in the "impurity band" invoked to explain the anomalous low-temperature electrical properties of germanium.[7] Our principal reasons for doubting this possibility are the observed doping proportionality of the intensity of these resonances, and the observation of the donor resonance in the same samples. We would expect the ratio of the number of electrons contributing to the two types of spectra to become markedly concentration-dependent when overlap effects become appreciable. However, this still seems the most likely possibility to the authors.

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[4]We are indebted to G. Reiland of Minneapolis Honeywell Regulator Co., W. F. Leverton of Raytheon Manufacturing Company, and G. Weinreich and H. G. White of Bell Telephone Laboratories for supplying the samples.

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[6]In correlating the area under the absorption curves with the number of electrons we have assumed non-degeneracy, i.e., the applicability of Curie's law to all resonances.

[7]See H. Fritzsche, Phys. Rev. 99, 406 (1955), for electrical properties, discussion, and references to earlier work.