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PARAMAGNETIC RESONANCE ABSORPTION FROM ACCEPTORS IN SILICON

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(Received August 24, 1960)

In the past, several attempts to observe the paramagnetic absorption from acceptors in silicon were unsuccessful. The reasons for this failure were pointed out by Kohn[1] and are associated with the degeneracy of the valence band in silicon. We wish to report in this Letter the observation of the paramagnetic resonance signal from p-type silicon subjected to a uniaxial stress which removes this degeneracy and thereby eliminates the difficulties encountered in previous experiments.

The structure of the valence band in silicon is shown in Fig. 1(a). In the absence of strains the bands are degenerate at $k=0$ and the energy surfaces are fluted as indicated at the bottom of Fig. 1(a). In the presence of a uniaxial stress the degeneracy is lifted and for large enough strains the bands become decoupled and ellipsoidal [see Fig. 1(b)]. Local random strains due to dislocations, imperfections, and lattice vibrations are always present in a sample and will split the valence band by an amount $\Delta E = DS$, where D is the appropriate deformation potential and S the internal strain. In an external magnetic field H, the spin degeneracy is also lifted and each band is split by the Zeeman energy $g_h \mu H$, where μ is the Bohr magneton and g_h the hole g value. We may distinguish the following two cases:

$\Delta E \approx g_h \mu H$: This situation is illustrated in Fig. 1(c). Since the bands are not characterized by a given M_J quantum number, all the six spin transitions indicated are allowed, which will result in a very short spin-lattice relaxation time. A sample with random internal strains will have a distribution of ΔE values and hence a multitude

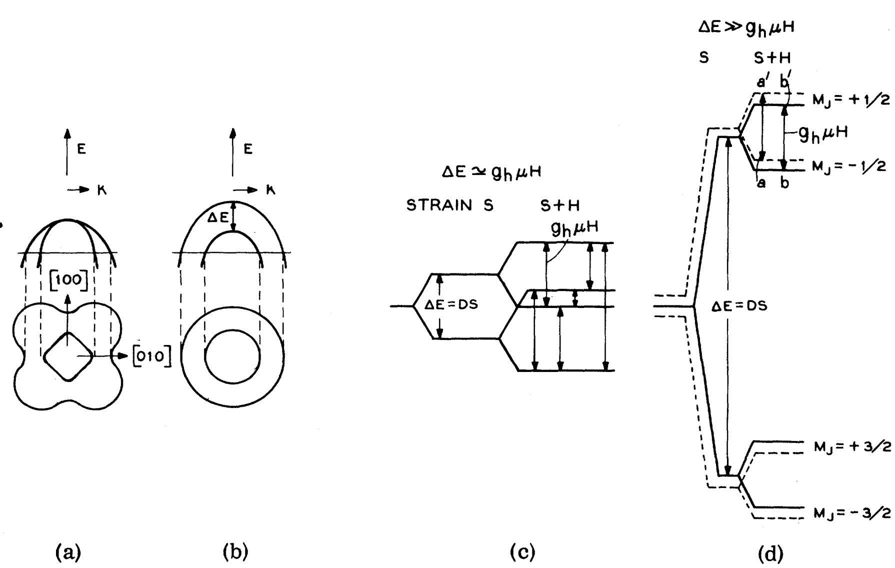

FIG. 1. Valence band in silicon: (a) in the absence of stress; (b) with applied uniaxial stress. (c) Energy levels with $\Delta E \approx g_h \mu H$. All six transitions indicated are allowed. Resonance line will be broadened and difficult to observe. (d) Energy levels with $\Delta E \gg g_h \mu H$. Transition frequencies $aa' = bb'$. Lines will not be broadened by random internal strains and paramagnetic resonance is observable.

of possible spin transitions with different effective g values. The resulting broadening of the resonance line will make its observation very difficult.

$\Delta E \gg g_h \mu H$: This situation can be easily realized by applying an external uniaxial stress to the sample. Figure 1(d) illustrates the case when the stress is applied along the [100] direction. The bands may be characterized by their M_J quantum numbers. The allowed spin transitions are $\Delta M_J = \pm 1$. The g values in this situation will be to first order strain-independent; the transitions $bb' \simeq aa'$, and therefore the internal strains will be ineffective in broadening the resonance line. This represents the situation under which the paramagnetic resonance absorption was observed.

The experiments were performed on a p-type silicon sample at 1.3°K and ~9000 Mc/sec. The external compressive stress was applied by means of a calibrated spring whose tension could be varied during the experiment. The experimental traces from a silicon sample with 1.5×10^{17} borons/cm^3 subjected to a stress in the [100] direction are reproduced in Fig. 2. The broadening of the line and its ultimate disappearance when the stress is removed is clearly observable.

The hole g value is anisotropic and can be fitted with the expression $g^2 = g_\perp^2 \cos^2\theta + g_\parallel^2 \sin^2\theta$, where θ is the angle between the stress axis and the external magnetic field. Figure 3 shows the experimental results obtained on different acceptors in silicon subjected to stresses of 700-900 kg/cm^2. The acceptor concentrations were approximately 10^{17} acc/cm^3. Boron-doped silicon was investigated in greater detail and the concentration was varied between 5×10^{15} and 2×10^{17} B/cm^3. The g values in this region were found to be concentration independent and for a stress T of 800 kg/cm^2 along the [100] direction had values of

$$g_\perp = 2.43 \pm 0.01, \quad g_\parallel = 1.21 \pm 0.01.$$

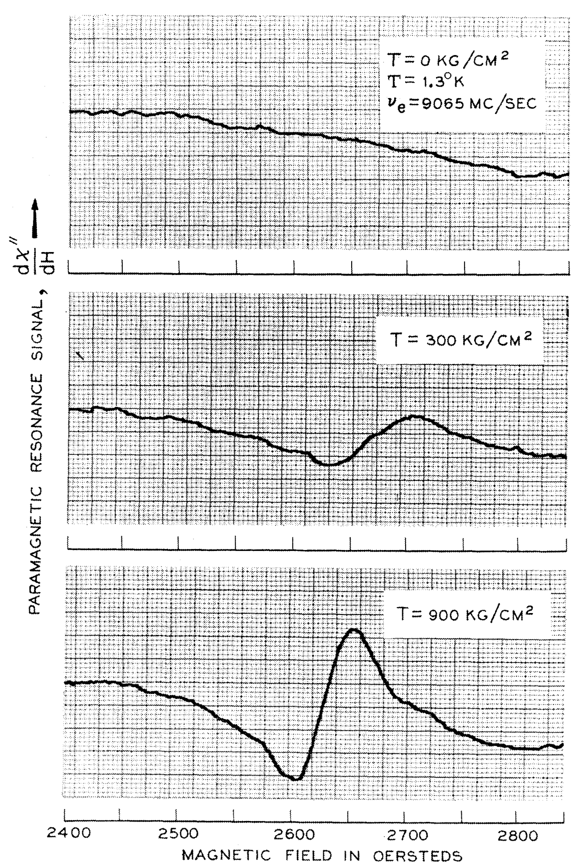

FIG. 2. Paramagnetic resonance absorption from holes in boron-doped silicon (1.5×10^{17} B/cm^3) subject to uniaxial stress. $T \parallel [100]$; $H \perp T$. Note the broadening and disappearance of the line as the strain is reduced. The residual signal at zero strain is due to a background resonance and is also present in an empty cavity.

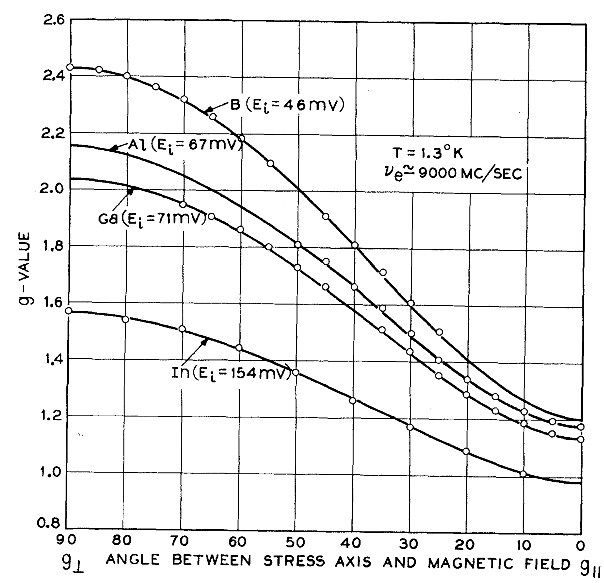

FIG. 3. g value vs angle for different acceptors in silicon. The acceptor concentrations were approximately 10^{17} acc/cm^3. A stress of 700-900 kg/cm^2 was applied in the [100] direction; the magnetic field was rotated in the (110) plane of the sample. Note the strong dependence of the g value on the binding energy[1] E_i of the hole. The solid line represents the theoretical fit, $g^2 = g_\perp^2 \sin^2\theta + g_\parallel^2 \cos^2\theta$. The lack of data along some parts of the curve is due to a background line which interfered with the acceptor resonance signal.

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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(Received August 26, 1960)

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

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

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

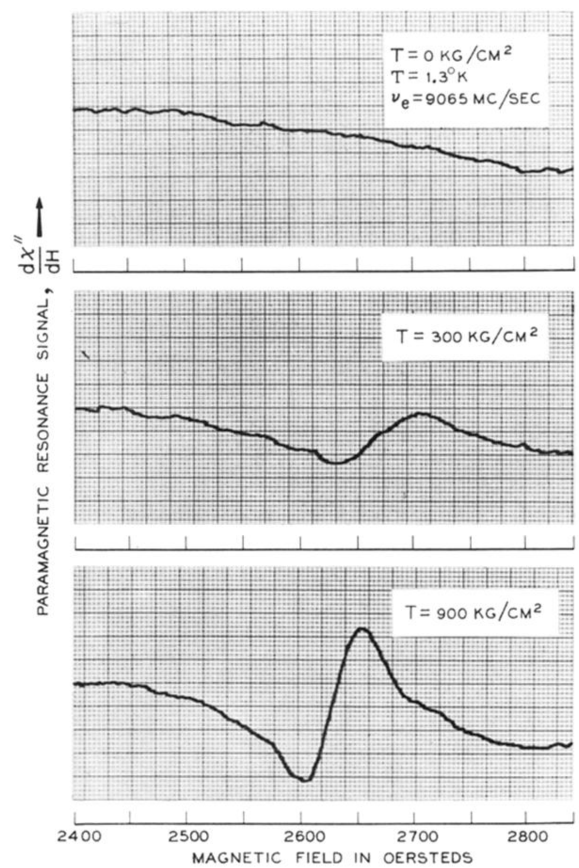

FIG. 2. Paramagnetic resonance absorption from holes in boron-doped silicon (1.5×10^{17} B/cm^3) subject to uniaxial stress. $T \parallel [100]$; $H \perp T$. Note the broadening and disappearance of the line as the strain is reduced. The residual signal at zero strain is due to a background resonance and is also present in an empty cavity.