Letters to the Editor

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Effect of Pressure on the Superconducting Transition Temperature of Thallium

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THE effect of pressure on the superconducting transition temperature of thallium has been investigated at pressures up to nearly 5000 kg/cm². Pressure was applied to the thallium by a piston and cylinder arrangement, using solid hydrogen as the pressure-transmitting medium, and the electrical resistance of the thallium was measured as a function of temperature. The experimental arrangement has been described in an earlier publication.[1]

The results of this preliminary study are shown in Fig. 1. The sharpness of the transitions, even at maximum pressure, suggests that the stress transmitted to the specimen is rather uniform. In Fig. 2 is shown the transition temperature *vs* pressure as derived from the curves of Fig. 1. At low pressures, we find $\partial T_c/\partial P \sim +1.2\times 10^{-5}$ deg/(kg/cm²), whereas for pressures greater than about 2500 kg/cm² we get $\partial T_c/\partial P \sim -0.43\times 10^{-5}$ deg/(kg/cm²). The transition temperature has a maximum at a pressure in the neighborhood of 1500 kg/cm². The values given for the pressure are calculated from the thrust on the piston and should be corrected for friction; this correction is not serious.

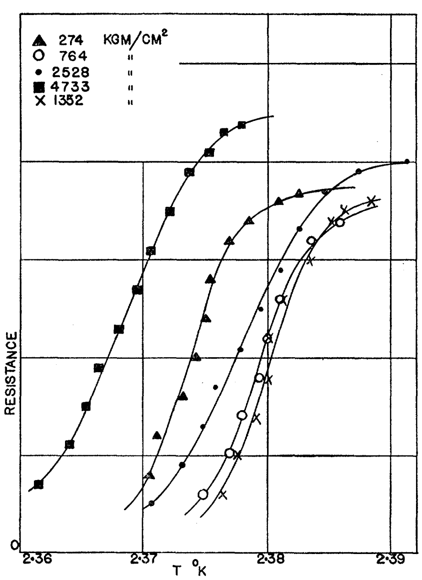

FIG. 1. Electrical resistance *vs* temperature for thallium at different pressures.

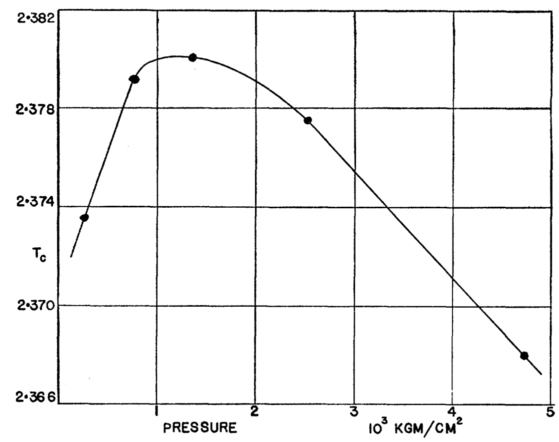

FIG. 2. Superconducting transition temperature of thallium *vs* pressure.

These results account for some of the wide disagreement between hitherto published values of $\partial T_c/\partial P$ for thallium.[2]

In the experiments reported here, the pressure-transmitting medium actually used was solid HD. The results obtained when solid H_2 was used showed a significant difference which we ascribe to the effect of pressure on the *ortho-para* conversion rate in solid H_2. It seems that this conversion rate increases appreciably with pressure, at least up to 2000 kg/cm², but no reliable quantitative data can yet be given.

Similar investigations have been made on a number of other superconductors and a more detailed report will be submitted for publication later.

Thanks are due Mr. Ray Sawyer for his assistance with the measurements.

[1] J. Hatton, Phys. Rev. **100**, 681 (1955).
[2] N. L. Muench, Phys. Rev. **99**, 1814 (1955) gives a convenient summary of published results for thallium.

Exchange Effects in Spin Resonance of Impurity Atoms in Silicon

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FLETCHER *et al.*[1] observed in the microwave resonance of donors in silicon weak satellite lines located halfway between pairs of the $2I+1$ main lines. The main lines arise from the hyperfine interaction of the electron with the magnetic moment of the donor atom, while the satellites originally were believed to

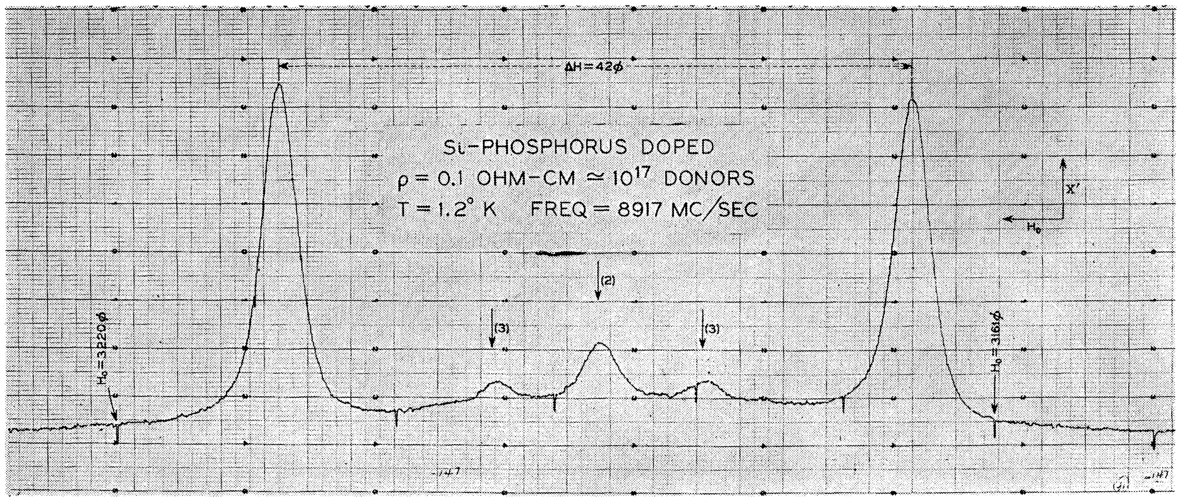


FIG. 1. Electron spin resonance lines in phosphorus-doped silicon under fast-passage conditions. Resistivity of sample 0.1 ohm cm. Small vertical lines are magnetic field markers.

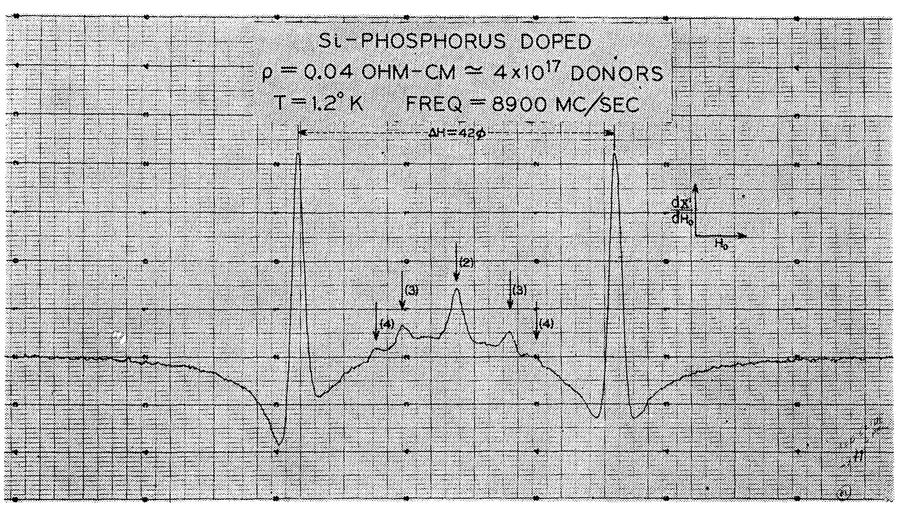
arise from a forbidden transition associated with the simultaneous flip of the electron and nucleus. Slichter[2] suggested that the satellite lines arise from the exchange coupling between two electrons which, acting as a unit, see the average field of the nuclei. The purpose of the present note is to confirm Slichter's theory by reporting the observation of additional lines attributable to an exchange between 2, 3, and 4 electrons.

The samples used were phosphorus-doped silicon with resistivities of 0.1 ohm cm and 0.04 ohm cm, respectively, cut from different crystals. Measurements were made at $\sim$9000 Mc/sec at a temperature of 1.2°K. By the phase unbalance of a microwave bridge, the equipment was made sensitive to the real part of the magnetic susceptibility. Magnetic field modulation, heterodyne microwave detection, and lock-in amplifier were used to record the resonance lines. The results obtained are shown in Fig. 1 and Fig. 2. The 0.1 ohm cm sample clearly shows the lines arising from the exchange between 2 and 3 electrons and the heavier doped 0.04 ohm cm sample between 2, 3, and 4 electrons. The places at which the lines should appear are indicated by the arrows, the numbers in parentheses referring to the number of donors in the cluster. The large background signal may arise from clusters which are larger in size or whose exchange interaction is comparable with the hyperfine interaction.

The electronic relaxation time of the 0.1 ohm cm sample is of the order of seconds and hence the shape is as expected for Bloch's fast-passage case.[3] The 0.04 ohm cm sample had a relaxation time of less than 10^{-5} second and shows the regular slow-passage line shape. The origin of the wide range of relaxation time is now being investigated.

A study of the amplitudes of the various satellites should shed light on the clustering of the atoms and

FIG. 2. Electron spin resonance line in phosphorus-doped silicon under slow-passage conditions. Resistivity of sample 0.04 ohm cm.



may help elucidate the onset of impurity band conduction.

We would like to thank P. W. Anderson for helpful discussions.

[1] Fletcher, Yager, Pearson, Holden, Read, and Merritt, Phys. Rev. **94**, 1392 (1954); Fletcher, Yager, Pearson, and Merritt, Phys. Rev. **95**, 844 (1954).
[2] C. P. Slichter, Phys. Rev. **99**, 479 (1955).
[3] F. Bloch, Phys. Rev. **70**, 460 (1946); A. M. Portis, Phys. Rev. **99** (1955).

Thermal Acceptors in Vacuum Heat-Treated Germanium

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(Received September 14, 1955)

We wish to describe an experiment in which it is found that very few acceptor centers are introduced into copper-free germanium by quenching from high temperatures. The result is of interest because the number of acceptor centers found in the present quenched specimens is far smaller than that reported previously for germanium.[1,2] We believe that these new results are obtained because greater care has been taken in maintaining the germanium surface free of impurities.

The bar of single-crystal germanium is heated in vacuum by passing a large alternating current through it, the temperature attained being measured by means of an optical pyrometer. The current leads are tantalum spot-welded to the germanium. Voltage probes are germanium side arms (continuous parts of the crystal) formed during the initial sample shaping procedure. The germanium is quenched from high temperature by shutting off the current and allowing the crystal to cool by radiation. The initial quenching rate of about 170°/sec (from 900°C) is comparable to (but somewhat faster than) Mayburg's radiation quench[2] and probably slower than Logan's oil bath quench.[1] The concentration of quenched-in acceptors is calculated from measured values of conductivity (at 195°K) combined with the mobility data of Prince.[3]

Some typical results are shown in Fig. 1 in which we plot the concentration of quenched-in acceptors as a function of temperature from which the germanium is quenched. Earlier results on copper-free germanium are also indicated.

It should be mentioned that because of the relatively small conductance changes measured in the present experiment, the increase in surface conductance with heating in vacuum as reported by Clarke[4,5] becomes an appreciable fraction of the total conductance change (about 25% for a crystal 0.07 cm in thickness). The increased surface conductance arises, in part, from desorption of oxygen. However, this surface conductance can be reduced to nearly its initial value either by means of readsorption of oxygen or by producing a new surface by means of brief etching.[4,5] This latter procedure was adopted here in order to estimate the surface contribution to the total conductance change.

The smallest concentration of quenched-in acceptors obtained after the surface cleaning procedure described below is 1×10^{13} centers/cm^3 at 894°C as shown on Fig. 1. The germanium sample was then recleaned under conditions thought to be identical to the first cleaning, and this was followed by further heat treatment. The result was an increase in acceptor concentration as shown also on Fig. 1. This lack of reproducibility can be regarded as a strong indication that the quenched-in acceptors correspond to impurities rather than to lattice defects.

Since the new results are thought to arise from the use of germanium samples with less contaminated surfaces, it is desirable to list the detailed handling procedure. After shaping and attachment of the current and voltage leads, the germanium is (1) etched in a solution consisting of 10 parts of HNO_3 conc. ACS and 1 part of HF 48% ACS, (2) rinsed three times in double demineralized water, (3) immersed for 1 hour in 10% KCN (ACS) aqueous solution (double demineralized water) to help remove copper and possibly other metallic ions,[1] (4) rinsed five times in double demineralized water, and finally (5) enclosed and under vacuum within two minutes after the final rinsing. The ger-

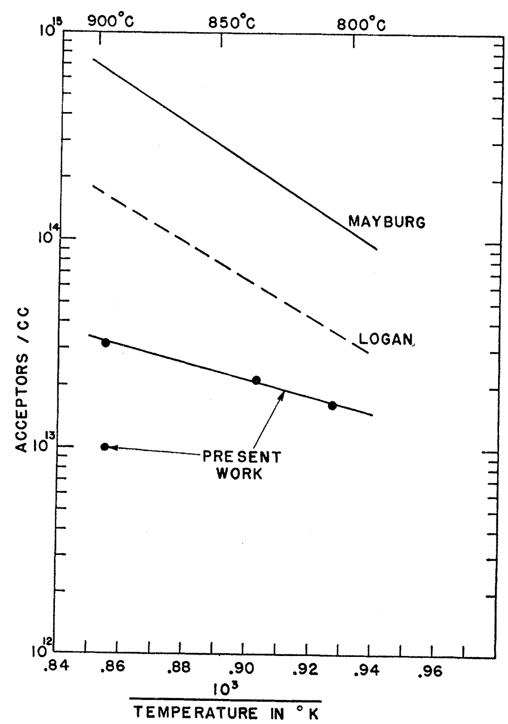

Fig. 1. Concentration of acceptors quenched into germanium after vacuum heat treatment at various temperatures as found by Mayburg, Logan, and present work.

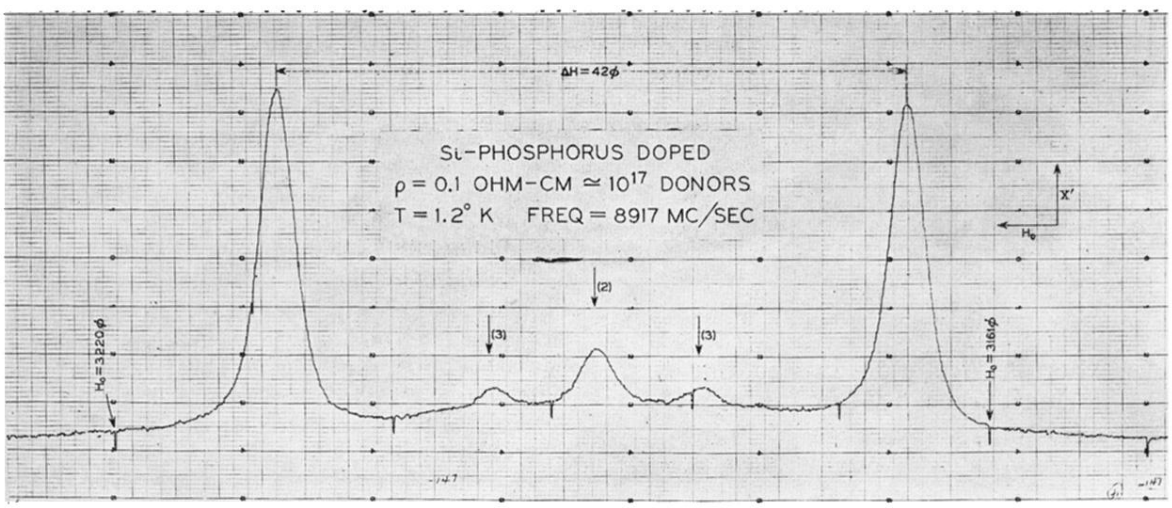

Fig. 1. Electron spin resonance lines in phosphorus-doped silicon under fast-passage conditions. Resistivity of sample 0.1 ohm cm. Small vertical lines are magnetic field markers.

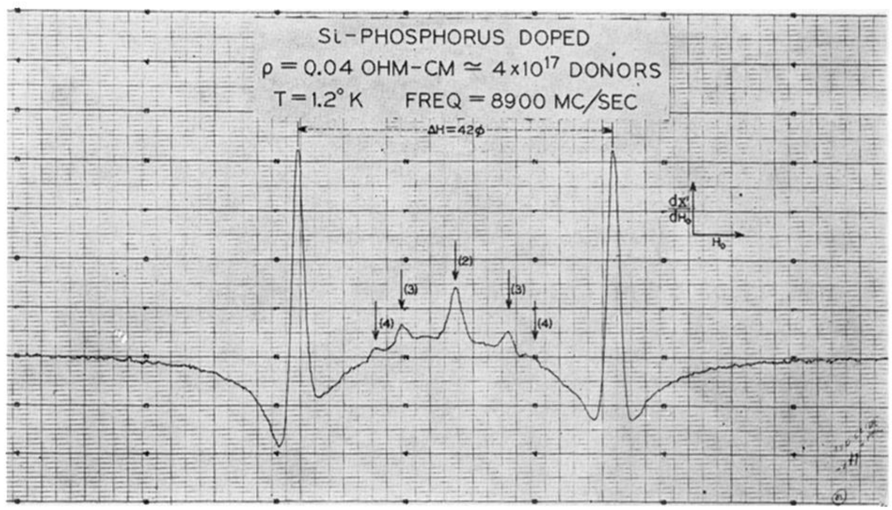

FIG. 2. Electron spin resonance line in phosphorus-doped silicon under slow-passage conditions. Resistivity of sample 0.04 ohm cm.