FIG. 1. Distribution coefficient of antimony in germanium.
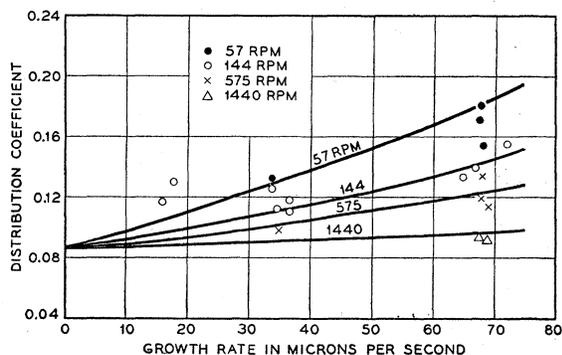

FIG. 2. Distribution coefficient of gallium in germanium.

shown in Figs. 1 and 2. It is seen that the distribution coefficient at a given growth rate decreases markedly with increased vigor of stirring, which demonstrates the importance of diffusion in the liquid. In particular, diffusion clearly is not negligible for a crystal rotation of 200 rpm, the rate used by Hall.

A theory has been developed[2] which takes account of the diffusion process in the melt and the nature of the fluid flow resulting from rotation of the crystal. If no cognizance is taken of effect (b), assuming instead that the ratio of the concentration in the solid to that in the melt at the interface is a constant K_0, then the theory leads to the following expression for the distribution coefficient K in the steady state:

$$K = \frac{K_0}{K_0 + (1 - K_0) \exp(-f\delta/D)}.$$

Here f is the growth rate and D is the diffusion coefficient of the solute in the melt. The parameter δ is a characteristic distance, measured from the interface, within which diffusion controls the transport of solute atoms away from the crystal. The theory predicts that δ varies inversely with the square root of the angular velocity of crystal rotation. The theory is fitted to experiment for one rotation rate. It is seen then that the theoretical curves agree fairly well with all the data, even though effect (b) has been ignored.

It may be true that effect (b) influences the distribution coefficient, but there is reason to believe that this influence is small, under the growth conditions in use. On the other hand, it is evident that the diffusion process in the melt has a profound effect upon the distribution coefficient.

[1] The distribution coefficient is defined as the ratio of the solute concentration in the solid to that in the bulk of the liquid from which crystallization is taking place. This ratio has also been termed the purification constant and the segregation constant.

[2] These matters were discussed by J. A. Burton at the Institute of Radio Engineers and American Institute of Electrical Engineers Conference on Semiconductor Device Research, June 1952, and will be dealt with more fully in a forthcoming publication by Burton, Prim, and Slichter.

[3] R. N. Hall, Phys. Rev. 88, 139 (1952).

[4] G. K. Teal and J. B. Little, Phys. Rev. 78, 647 (1950).

Electron Spin Resonance in a Silicon Semiconductor*

A. M. PORTIS, A. F. KIP, AND C. KITTEL, Department of Physics, University of California, Berkeley, California

AND

W. H. BRATTAIN, Bell Telephone Laboratories, Murray Hill, New Jersey

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WE have observed electron spin resonance absorption in the 9000 Mc/sec range in a powdered n type silicon semiconductor specimen at temperatures between 4°K and 300°K. We believe this is the first occasion that electron spin resonance has been reported for a semiconductor. The preliminary results suggest that the resonance method will be a useful tool for the study of impurity and conduction electron states in semiconductors.

The silicon was prepared by the Bell Telephone Laboratories through the courtesy of S. O. Morgan, E. Buehler, and J. H. Scaff. A crystal of resistivity between 0.01 and 0.02 ohm-cm was grown with the addition of 1×10^{18} to 2×10^{18} phosphorous atoms/cm^3 to high purity du Pont silicon. The crystal was crushed in a steel die, washed overnight in HF, and sieved through a 325 mesh screen. Microscopic examination indicates that almost all the particles have diameters under 10 microns. The calculated skin depth at room temperature is about 100 microns. We suspended the particles in paraffin wax of insulation. The test specimen contained about 0.2 cm^3 of Si.

The g factor is 2.001 ± 0.001, independent of temperature between 4°K and 300°K. The line width at half-maximum absorption is plotted against temperature in Fig. 1. The shape of the line is Lorentzian. Saturation effects could not be obtained with the klystron source, from which we are able to conclude that the
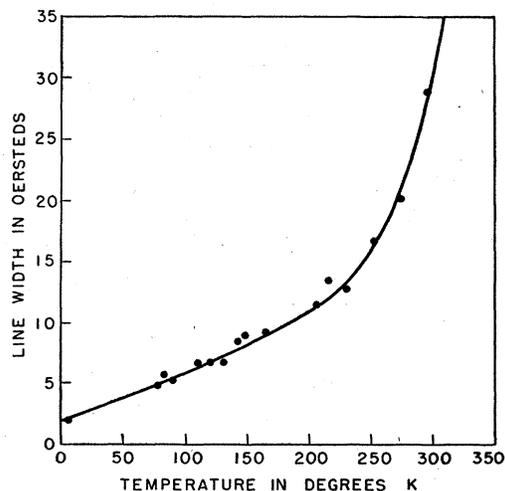

FIG. 1. Line width at half-maximum absorption vs temperature.

spin-lattice relaxation time at 4°K is less than $\sim 10^{-3}$ sec. The temperature dependence of the line width is baffling. The calculated dipolar width taking the electron spins at rest is only 0.1 oersted. The possible hyperfine interactions are with the phosphorous atoms and with the isotope Si^{29} which is about 5 percent abundant, but because of motional narrowing it seems impossible to account for the width in this way. Surface recombination of electrons and holes does not appear to be a sufficiently rapid process.

The susceptibility data plotted in Fig. 2 were obtained from a comparison of the integrated intensity of the absorption with that of a crystal of $CuSO_4\cdot 5H_2O$. The relative accuracy of the point
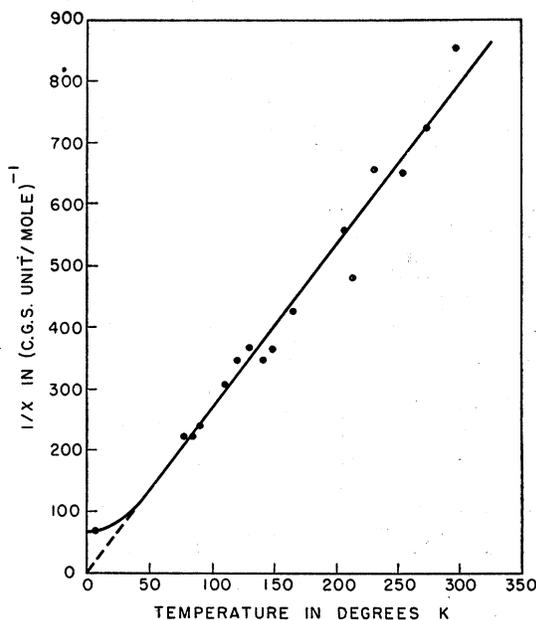

FIG. 2. Reciprocal paramagnetic susceptibility vs temperature.

at 4°K is quite good; we therefore conclude that the transition from Langevin (nondegenerate) paramagnetism to Pauli (degenerate) paramagnetism is exhibited experimentally by these results. The slope of the high temperature portion of the $1/\chi$ vs T curve suggests that the electron concentration is $(1.5\pm 0.1)\times 10^{18}$ per cm^3. This figure is compatible with the concentration of phosphorous atoms. It may be noted that the susceptibility determined in a spin resonance experiment is essentially the pure paramagnetic susceptibility without significant disturbance from diamagnetic contributions. It will be of interest to determine the diamagnetism of the conduction electrons by subtracting the rf resonance susceptibility from the static susceptibility.

The theoretical free electron degeneracy temperature T_0 for the observed concentration of electrons is 56°K, using a one-band model. The observed susceptibility value at 4°K leads to an observed $T_0=38$°K. On a one-band model we would therefore have $m^*/m=1.5$. Dr. Herring has pointed out that the possible degeneracy of the conduction band[1] in silicon, if one supposes that there are six degenerate spherical energy surfaces in k space, would reduce our effective mass estimate to $m^*/m=(1.5)(1/6)^{\frac{2}{3}}=0.45$, a value in fair agreement with mobility data[2] for bulk polycrystalline silicon. These preliminary results thus give some support to the six-minima degenerate band model.

There is no evidence in our measurements for the existence of discrete impurity states below the bottom of the conduction band. This is consistent with the finding of Pearson and Bardeen that the activation energy of n type impurity atoms is already zero at a carrier concentration slightly below that of our specimen.

Our results, however, might be compatible with the two-band model of James and Ginzbarg.[3]

No resonance was observed at room temperature in high resistivity silicon (~ 8 ohm-cm). Magnetoresistive effects were observed, however. With our present sensitivity we should not not have expected to find a resonance here because of the low carrier concentration. This negative result supports our interpretation of the measurements on the n type specimen as associated with authentic volume effects.

The electrical losses vary in an unusual manner with the resistivity ρ. The electric field E_i inside an ellipsoid is related to the applied rf field E_0 by the relation

$$E_0/E_i = 1 + N\chi_0 - i(N/\rho\omega),\qquad (1)$$

where N is the demagnetizing factor and χ_0 is the static dielectric susceptibility. We have supposed that the particle size is much smaller than the rf skin depth. In many cases of interest in semiconductors the term $-iN/\rho\omega$ is dominant, and it is readily established that in this limit the Q of a particle is $\approx N^2/8\pi\rho\omega$. We see that in this limit the Q is lower the higher the resistivity of the material. This effect is observed. At 9000 Mc/sec the Q should improve after the resistivity exceeds 13 ohm-cm; this has also been observed qualitatively at low temperatures.

Professor W. F. Giauque kindly expedited the installation of his new helium liquifier and generously supplied us with liquid helium. We have benefited from helpful discussions with E. Conwell, F. Herman, C. Herring, H. M. James, and F. Seitz.

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[1] F. Herman, Phys. Rev. 88, 1210 (1952); F. Herman and J. Callaway. Phys. Rev. 89, 518 (1953); Dr. Herman (private communication) suggests from his calculations for diamond and germanium that the energy surfaces of the conduction band have six minima somewhere within the reduced zone along the (100) axes; the energy surfaces near these minima are nearly ellipsoids of revolution. The hole states have three nearly spherical energy surfaces with the maxima at k =000.
[2] G. L. Pearson and J. Bardeen, Phys. Rev. 75, 865 (1949); no really reliable effective mass values for silicon are yet available, the polycrystalline results being known to be seriously in error.
[3] A. S. Ginzbarg, thesis, Purdue University, 1949 (unpublished).

Second Sound Velocity in He^3—He^4 Mixtures Below 1°K*

J. C. KING AND HENRY A. FAIRBANK
Sloane Physics Laboratory, Yale University, New Haven, Connecticut
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MEASUREMENTS have recently been made of the velocity of second sound in mixtures of He^3 and He^4 in the temperature region obtained by adiabatic demagnetization of a paramagnetic salt. This is a preliminary report of our findings. A more detailed account of the experiment will follow in a final paper.

In previous measurements Lynton and Fairbank[1] showed that small amounts of He^3 substantially increased the velocity of second sound in the region above 1°K in agreement with the predictions of Pomeranchuk.[2] Below 1°K Pomeranchuk and Dingle[3] predict diametrically opposite behavior. Dingle suggests that for dilute mixtures of He^3 in He^4 the second sound velocity will rise to the same high value, $u_1/\sqrt{3}$, ($u_1=$velocity of first sound) as for pure He^4, whereas Pomeranchuk believes that for these mixtures a maximum in the velocity will be reached with a subsequent decrease to a small finite value at 0°K. Our results are in general agreement with the predictions of Pomeranchuk.

The velocity measurements were made using a single pulse technique.[1,4,5] The second sound cavity, made of copper 8.54 mm in length and 2.8 mm in diameter, employed a carbon disk resistor at either end for transmitting and receiving the second-sound pulse. The cavity was thermally connected to a pressed chromium potassium sulfate pill. A $\frac{1}{2}$-watt carbon resistor in turn was thermally connected to the copper cavity and used during the runs as a secondary thermometer. This resistor had been