

fine levels having total angular momentum values of $F=5/2$, $3/2$, and $1/2$. All of the Zeeman transitions ($\Delta F=0$, $\Delta m_F=\pm 1$) and all of the π hyperfine transitions ($\Delta F=\pm 1$, $\Delta m_F=\pm 1$) have been observed. Typical resonance curves are shown in Fig. 1. The resonances have a half-width of about 4 kc/sec. The identification of the various hyperfine transitions was facilitated by observation of their field dependence. In all cases the observed field dependence agreed within 1% with the theoretical values for the nitrogen resonances. The values obtained for the (5/2-3/2) and the (3/2-1/2) intervals are

$$\nu_{5/2, 3/2} = 26.1275 \pm 0.0005 \text{ Mc/sec,}$$

$$\nu_{3/2, 1/2} = 15.6772 \pm 0.0005 \text{ Mc/sec.}$$

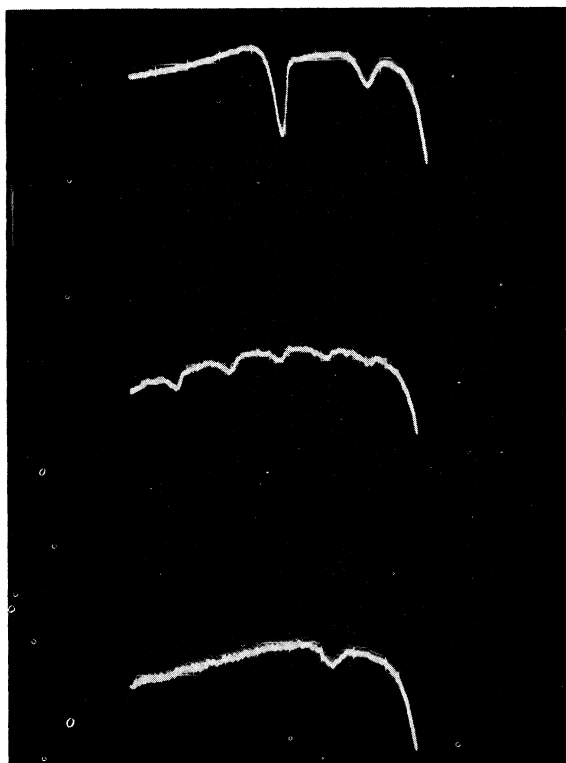


FIG. 1. Resonances observed in atomic nitrogen. The spike at the right-hand end of all of the traces is caused by the rf discharge used to dissociate the N_2 molecules. The duration of each of the traces is 1 sec.

Upper trace, Zeeman resonances in the $F = 5/2$ and $F = 3/2$ states as observed in a field of 0.1 gauss.

Middle trace, splitting of the $F = 5/2$ Zeeman resonance into its five components in a field of 1.0 gauss.

Bottom trace, hyperfine transition between the (3/2, -1/2) and (1/2, 1/2) states.

These values include a small correction for Zeeman curvature (typically 1 kc/sec). A search was made for a possible pressure shift by observing one of the hyperfine transitions as the pressure was reduced by a factor of two. It was established that if a pressure shift exists, it is less than 1 kc/sec over the range of pressures studied. The quoted uncertainties are about three times the probable error and are intended to allow for the possibility of a small pressure shift.

The value of the hyperfine interaction constant (a) obtained from the (5/2-3/2) transition is 10.4510 ± 0.0002 Mc/sec while that obtained from the (3/2-1/2) transition is 10.4515 ± 0.0003 Mc/sec. Both of these results are in excellent agreement with Heald and Beringer's² value of 10.45 ± 0.02 Mc/sec. The apparent discrepancy of the values of the interaction constant obtained from the two transitions may result from configuration mixing or interaction with the close-lying 2P and 2D states.

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MICROWAVE SPIN ECHOES FROM DONOR ELECTRONS IN SILICON

J. P. Gordon and K. D. Bowers
Bell Telephone Laboratories,
Murray Hill, New Jersey
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With the introduction of the spin-echo technique by Hahn,¹ it became possible to observe and measure directly transverse relaxation times T_2 in substances where the resonance lines involved were inhomogeneously broadened by local field variations. The spin-echo technique has been applied in the radio-frequency region both to nuclear spin resonances,² and more recently

to electron resonances in sodium-ammonia solutions.³ It was suggested by Feher⁴ that spin echoes from donors in silicon at microwave frequencies could be useful for finding the homogeneous part of line widths ($\Delta H_{\text{homogeneous}} \sim 2/\gamma T_2$, where $\gamma = 1.76 \times 10^7$ gauss⁻¹sec⁻¹ is the gyromagnetic ratio of the electron), and also that the enhanced signal to noise ratio, storage capacity, and speed of response obtained by going to microwave frequencies would make a spin-echo device a potentially useful memory.

We have made measurements at 23 kMc/sec on some samples of silicon at 1.4°K containing lithium and phosphorus, and found transverse relaxation times⁵ varying from 200 to 520 microseconds, depending somewhat on impurity concentration, on the type of donor, and on the isotopic purity of the host silicon crystal. On the basis of these measurements, one may envisage a memory device⁶ in which each element can store more than 10^4 bits of information.

A standard *K*-band heterodyne paramagnetic spectrometer was used for the measurements, as illustrated in simplified form in Fig. 1 (the simplification consists mainly of omitting the stabilization circuits of the klystrons). The necessary microwave pulses were generated by applying short positive voltage pulses to the repeller of the signal klystron. The klystron normally operated at a frequency 14 Mc/sec above the resonant frequency of the cavity, stabilized

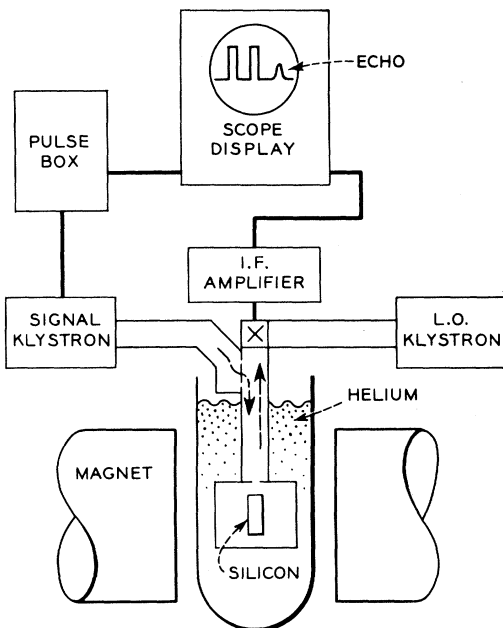


Fig. 1. Apparatus used for spin-echo measurements.

there by a rather slow-acting signal derived from a crystal via a multiplier chain. The pulses momentarily shifted the klystron's frequency down to coincide with the cavity, but were sufficiently short so that the stabilizer would not follow them.

Two identical microwave pulses were applied to the silicon sample; each was $\sim 1/4$ milliwatt in amplitude and ~ 2 microseconds in duration, making it approximately a "90° pulse." When the dc magnetic field was brought to resonance, one or two echo signals appeared following the two input pulses, as shown in Fig. 2 (the first echo also acts as a pulse, and generates a second echo). The measurement consisted of observing the amplitude of the first echo as a function of the time interval between the two input pulses.

Four samples of silicon were tested, each $\sim 1/10$ cm³ in volume, and the results are tabulated in Table 1. The samples varied in donor concentration, in type of donor, and in the host crystal, but all gave similar values of T_2 . The longest time was found in a sample of isotopically enriched silicon 28,⁷ but this was only a factor of two longer than the others.

It can be seen that T_2 decreases only slightly with increased donor concentration. The most notable change in T_2 was observed on going to the isotopically enriched Si²⁸ sample. In this sample the full line width was only 0.2 oersted, compared to 2.8 oersteds for natural silicon. We might expect this to be equivalent to an increase in spin concentration, resulting in a smaller T_2 . The fact that T_2 actually increases in this sample suggests that the Si²⁹ nuclei are at least partly responsible for the loss of phase memory of the spins.

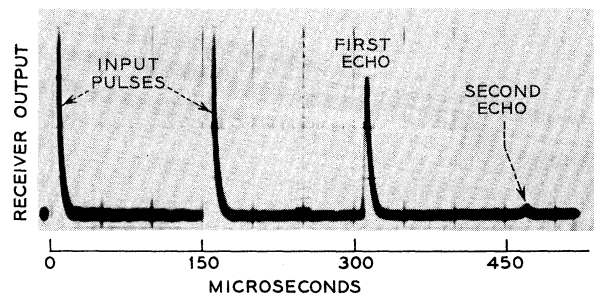


Fig. 2. Oscilloscope photograph of spin-echo signals. Two input pulses and two echoes are shown. The first echo doubles as an input pulse to generate the second echo. The width of the pulses is determined by the response time of the detection set.

Table I. Experimental results.

Sample	Type	Concentration of donors (cm ⁻³)	Spin-lattice time T_1 (sec)	Phase memory time T_2 (sec)
1.	P donors	3×10^{16}	~ 100	2.4×10^{-4}
2.	P donors	10^{17}	~ 1	2.0×10^{-4}
3.	Li donors	3×10^{16}	~ 100	2.4×10^{-4}
4.	P donors in isotopically enriched Si ²⁸	4×10^{16}	~ 50	5.2×10^{-4}

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⁵The transverse relaxation times T_2 given here are the time intervals between the first input pulse and the echo whose amplitude is down to $1/e$ of its maximum. The echo, as a function of the time interval between the first pulse and the echo (twice the interval between input pulses) appeared to have more nearly the Gaussian form $\exp(-kt^2)$ than the exponential e^{-kt} .

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PIEZORESISTIVITY IN REDUCED SINGLE-CRYSTAL RUTILE (TiO₂)

Lewis E. Hollander, Jr.
Lockheed Missile Systems Division,
Palo Alto, California
(Received September 22, 1958)

The effect of stress on the resistivity of reduced titanium dioxide single crystals, of the rutile structure, has been investigated. An increase in the resistivity with increasing tension was observed in these crystals. To the author's knowledge such an effect has not previously been reported for TiO₂. A study of this effect should contribute to the understanding of the conduction mechanism in rutile and other oxide semiconductors. In addition, there may be high-temperature transducer applications.

Rutile is an n -type semiconductor with a band

gap energy of 3.05 ev. Single crystals, fully oxidized, are normally light yellow in color and have a resistivity as high as 10^{13} ohm cm. A deficiency of oxygen in the TiO₂ lattice creates oxygen vacancies which increase the optical absorption and reduce the resistivity. For high oxygen-vacancy densities, the material appears deep blue and can have a resistivity as low as 0.1 ohm cm.^{1,2} The rutile crystal structure is tetragonal,³ with $a = 4.4923\text{\AA}$ and $c = 2.8930\text{\AA}$ and the Schonflies symmetry, D_{4h} .

Preliminary isothermal measurements were made of the longitudinal piezoresistive coefficients in directions both parallel and perpendicular to the c axis of the reduced TiO₂ crystal. The orientation of the c axis of the crystal was inferred from the orientation of the seed crystal and the preferred direction of growth of the TiO₂ boule. The orientation of the other crystal axes was unknown. Samples, $1.5 \times 0.2 \times 0.2$ cm, were cut from boules of pure TiO₂ about 3 cm high and 1.5 cm in diameter.⁴ Pure, clean, indium electrodes were soldered directly to the carefully cleaned TiO₂ crystals. The resistivity of these samples was 0.7 ohm cm in a direction parallel to the c axis and in the order of 2 ohm cm perpendicular to the c axis. A stress of approximately 2.5×10^7 dynes/cm² was applied with a beam balance, and the potential was measured with a Leeds and Northrup potentiometer.

The piezoresistive effect may be expressed as a fourth-rank tensor which, for the D_{4h} crystal symmetry of rutile, has six piezoresistive coefficients. These consist of the four longitudinal coefficients, π_{11} , π_{12} , π_{13} , π_{33} , and the two shear coefficients π_{44} and π_{66} .

The longitudinal piezoresistive coefficient, π_l , was determined from the relation

$$\pi_l = \frac{\Delta\rho}{\rho_0 X} = \frac{\Delta R}{R_0 X} - (S_{33} - 2S_{13}).$$

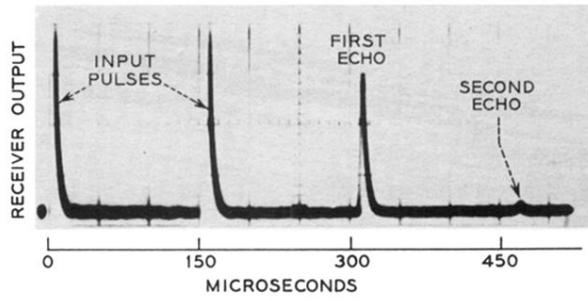


Fig. 2. Oscilloscope photograph of spin-echo signals. Two input pulses and two echoes are shown. The first echo doubles as an input pulse to generate the second echo. The width of the pulses is determined by the response time of the detection set.