

to the surroundings at room temperature. This heating and quenching in a high vacuum may have produced a surface cleaner than the original etched surface, but also has changed the bulk characteristics. As described below, the germanium appears now to be more sensitive to surrounding gases than was the original crystal with etched surface.

After the above heating and quenching, gases at several different pressures were admitted slowly through the vacuum system. Figure 1 shows a typical plot of germanium conductance at 197°K varying as the residual gas pressure varies from 10^{-7} mm Hg to 10^{-3} mm Hg (by shutting off the diffusion pump). Dry argon admitted to the germanium at 0.3 mm Hg for one minute has little effect upon the conductance but dry oxygen at 0.3 mm Hg for one minute increases the conductance by a factor of ten. The largest surface conductance at 197°K obtained during similar observations is 8×10^{-4} mho, representing about 10^{13} carriers per

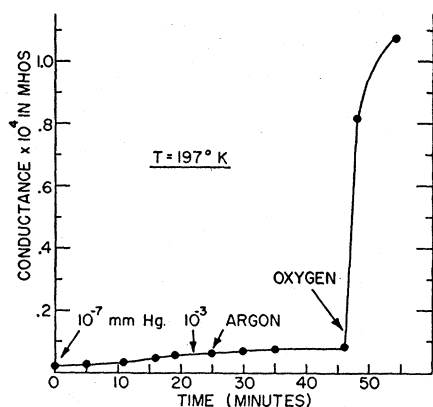


FIG. 1. Dependence of Ge conductance upon surrounding atmosphere. The diffusion pump was shut off at time $t=0$; argon was admitted at $t=25$ min and removed after one min; oxygen was admitted at $t=47$ min and removed after one min.

cm^2 of surface (if a mobility of $1000 \text{ cm}^2/\text{volt sec}$ is assumed). Oxygen is also adsorbed at room temperature. Initially, it appeared possible to remove most of the absorbed gas (as measured by electrical conductance) by simply heating the experimental tube containing the Ge in a high vacuum at about 450°C for one half-hour. However, Fig. 2 shows that as the number of cycles increased (each cycle corresponding to a maximum conductance with gas adsorption and then a minimum conductance after heating in a high vacuum), the minimum conductance became larger. By the twelfth cycle, heating the tube at 450°C had a much smaller effect in reducing the surface conductance. This might be

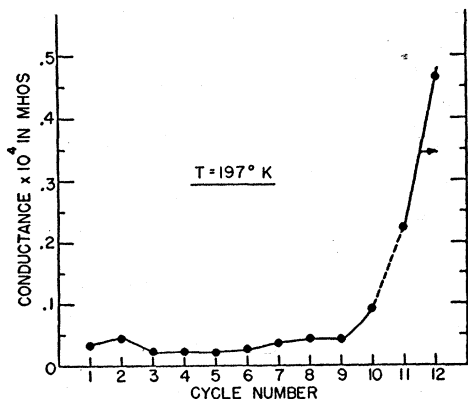


FIG. 2. Conductance of Ge after heating in high vacuum. Each cycle corresponds to a maximum and minimum conductance. Cycles 11 and 12 correspond to right-hand ordinate.

described in terms of a thin layer (oxide) being built up on the surface. It is not unreasonable to assume that oxygen may introduce surface acceptor energy levels resulting in hole conductivity.

Further work will include measurements to determine surface carrier type and surface mobility of carriers.

¹ N. F. Mott, Proc. Inst. Elect. Engrs. (London) 96, 253 (1949).

Thermally Induced Acceptors in Single Crystal Germanium

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WHEN germanium is heated above 600°C and then cooled, it has been shown¹ that the acceptor density increases markedly. This effect is reversible in that prolonged reheating at 475°C "anneals" out these acceptors. More recently, similar acceptors have been produced in experiments² where the cooling time has varied from a very rapid quench to a time of the order of several minutes.

It has been shown³ that copper as an impurity in germanium has the same activation energy, diffusivity, solid solubility, and "annealing" property as these acceptors. Since no precautions were taken to avoid copper contamination, and since very small concentrations of copper will produce these acceptors, this evidence led to the conclusion³ that in all of the above experiments copper produced the observed acceptor centers. A method has been developed by which it is possible to heat germanium to high temperature for extended periods of time and avoid copper-like contamination. This makes it possible to examine more closely the phenomena associated with quenching germanium from high temperature.

In these experiments, small samples were cut from single crystal n -type germanium which contained about 6×10^{12} donors per cc. The specimens were cleaned⁴ by acid etching followed by a rinse in twice-distilled water. They were then soaked in a strong aqueous KCN solution. The cyanide forms soluble complexes with copper, as well as other metallic ions, which are then removed by rinsing the specimens in twice-distilled water.

To study the effect of rapid quenching from high temperatures, a sample was placed on a carbon boat furnace in a quartz tube and heated in a hydrogen atmosphere by rf induction. A castor oil bath was located about one inch below the boat. The sample could be dropped from the boat into the oil bath in about 0.1 second. If one of the samples was heated at an elevated temperature for one minute and allowed to cool slowly to room temperature by simply turning off the rf heater, no detectable change in resistivity occurred. Resistivity was measured at -78°C , where the measurement was sensitive to impurity concentrations as low as a few times 10^{12} per cc or about one per 10 billion germanium atoms. In this experiment, the sample cooled to 500°C in about 15 seconds and reached room temperature in a few minutes (hereafter this will be referred to as the regular cooling cycle). However, if the sample was quenched in the oil bath, a change in resistivity resulted and acceptor centers were found uniformly throughout the sample. The effects of heating at different temperatures before quenching are shown in Fig. 1.

If the quenched samples were recleaned, as described above, and reheated to a high temperature followed by the regular cooling cycle, they returned to nearly their original resistivity.

It has been proposed⁵ that lattice defects such as vacancies and interstitial germanium atoms may act as acceptors in germanium. If the acceptor centers produced by quenching are thermally produced lattice defects,⁶ then to a close approximation the density of acceptor centers n_Q present when the sample is in thermal equilibrium at temperature T_Q is given by

$$n_Q = n_L e^{-E/kT_Q}$$

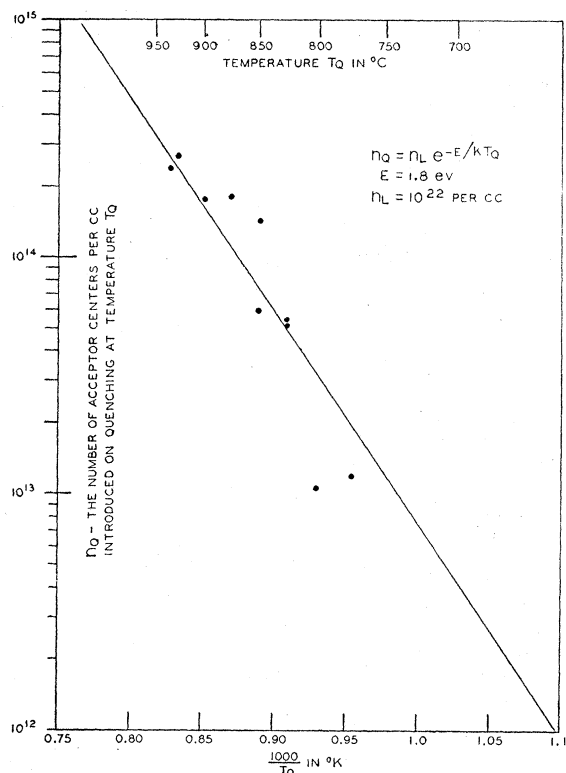


FIG. 1. Temperature dependence of acceptor concentration in quenched germanium samples.

where E is the activation energy for the production of an acceptor center and n_L is the maximum density of lattice sites that could be occupied by acceptors of this type. From theory,⁷ n_L is approximately 10^{22} per cc for germanium. If the equilibrium state of the sample at temperature T_Q is essentially "frozen" by the rapid quench, the measured increase in acceptor center density should be very nearly equal to n_Q . In the limit of $T \rightarrow \infty$, the curve is made to pass through $n_Q = n_L$ as required theoretically. The activation energy is found to be 1.8 eV per center, which may be compared to the activation energy of 1.2 eV per center for the introduction of copper into the germanium lattice.³

If the thermally produced acceptor centers are due to some unknown chemical impurity, then Fig. 1 can be regarded as a plot of the temperature dependence of the solid solubility of this impurity in germanium. There are two ways in which impurities could enter a quenched sample. They could diffuse into the germanium during the quench, although no impurity whose diffusion in germanium has thus far been studied could diffuse uniformly from the surface in this short time. A more likely possibility is that an impurity has diffused into the germanium during the heating time, and that the rapid quench has essentially "frozen" this dispersed impurity which would otherwise "anneal" in the regular cooling cycle. This "annealing" might be similar to (though much faster than) that for copper in germanium. There is, as yet, insufficient evidence to distinguish lattice defects from chemical impurities.

Although the surface treatments described above permit the heating of a test sample to high temperature without resistivity change, there was always a decrease in body lifetime. For example, when a test sample with an original lifetime of $100\mu\text{sec}$ was heated for one minute at about 825°C , followed by the regular cooling cycle, the average body lifetime was reduced to $19\mu\text{sec}$. It is known that recombination centers are formed by some chemical impurities⁸ and by lattice imperfections.⁹ In the heat

treatments performed in these experiments, the cause of the recombination centers has not been ascertained. The preliminary experiments indicate that recombination centers diffuse in rapidly from the surface in a manner similar to copper. This suggests that, in this case, recombination centers may be a chemical impurity which has a marked effect on lifetime while making only a small contribution to the resistivity.

I would like to express appreciation to W. Shockley, M. Sparks, and G. C. Dacey for encouragement in these experiments.

¹ H. C. Theuerer and J. H. Scaff, *Trans. Am. Inst. Mining Met. Engrs.* **191**, 59 (1951); Fuller, Theuerer, and van Roosbroeck, *Phys. Rev.* **85**, 678 (1952).

² W. E. Taylor, *Phys. Rev.* **86**, 642 (1952); C. Goldberg, *Phys. Rev.* **88**, 920 (1952); L. Esaki, *Phys. Rev.* **89**, 1026 (1953).

³ C. S. Fuller and J. D. Struthers, *Phys. Rev.* **87**, 526 (1952); W. P. Slichter and E. D. Kolb, *Phys. Rev.* **87**, 527 (1952).

⁴ This cleaning process was developed in collaboration with M. Sparks.

⁵ Lark-Horovitz, Bleuler, Davis, and Tendam, *Phys. Rev.* **73**, 1256 (1948).

⁶ Such defects have been observed in gold by J. W. Kauffman and J. S. Koehler, *Phys. Rev.* **88**, 194 (1952).

⁷ N. F. Mott and R. W. Gurney, *Electron Processes in Ionic Crystals* (Oxford University Press, London, 1940), Chap. II.

⁸ I am indebted to J. A. Burton for communication of these results prior to publication. They will be presented at the Joint Am. Chem. Soc.-Am. Phys. Soc. Symposium on Impurity Phenomena on June 16, 1953 (to be published in *J. Phys. Chem.*).

⁹ G. L. Pearson (private communication); also, W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 347.

Examples of Multiple Pion Production in n - p Collisions Observed at the Cosmotron*

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ABOUT 100 events attributed to π -meson production by neutrons in hydrogen have been photographed under conditions described in a previous communication.¹ Neutrons produced in a carbon target by the 2.2-Bev proton beam in the Cosmotron passed through appropriate collimators into a hydrogen-filled diffusion cloud chamber located in a field of 11 000 gauss. Two examples of creation of pairs of pions in the gas are shown in Figs. 1 and 2. Data on these events are given in Table I.

Track c in event A can be attributed to a proton from its momentum and estimated ionization density which are given in Table I. Tracks a and b , by the same method, must have been produced by particles much lighter than protons, most probably pions. (Masses of a and b are <400 and <240 electron masses, respectively.) The 6 angles fixing the directions of the 3 tracks with respect to the direction of travel of the incident neutrons were also determined by reprojecting the stereoscopic photographs in space. The resultant p_r of the transverse components of the three momenta is given in Table I. The fact that p_r is not zero also indicates that at least one neutral particle must be involved in addition to the charged ones, which is assumed to be a neutron. The two pions are then produced in the reaction $n + p = n + p + \pi^+ + \pi^-$.

TABLE I. Data on pion-pair events.

		Event A	Event B
Track a (negative charge)	Momentum (Mev/c)	474 ± 50	980 ± 70
	Estimated Ionization density	$1 \times \text{minimum}$	$1 \times \text{minimum}$
Track b (positive charge)	Momentum (Mev/c)	286 ± 20	550 ± 40
	Estimated Ionization density	$1 \times \text{minimum}$	$1 \times \text{minimum}$
Track c (positive charge)	Momentum (Mev/c)	835 ± 50	1260 ± 200
	Estimated Ionization density	1.5 to $2 \times \text{minimum}$	2 to $3 \times \text{minimum}$
Resultant transverse momentum, p_r (Mev/c)		268 ± 20	50 ± 60
Sum of forward momenta, p_s (Mev/c)		1260	2770
Sum of energies of charged particles (a, b, c), E_m (Mev)		1140	1950
Energy of incident neutron, E (Mev)		2060 $\begin{smallmatrix} +140 \\ -250 \end{smallmatrix}$	1980 ± 250