

FIG. 6. Ratio of photo-neutron yields with 18-Mev and 22-Mev bremsstrahlung spectra.

For the sake of simplicity we now assume that the resonance is narrow. Then the yield $Y \propto N_{\text{RES}} \int \sigma dE \propto N_{\text{RES}} A$ but $N_{\text{RES}} \propto 3(A/A_0)^{1/6} - 2$, where A_0 is the atomic number for which the resonant energy, $h\nu_{\text{RES}}$, is equal to the upper limit of the bremsstrahlung spectrum, E . Then $Y \propto [3(A/A_0)^{1/6} - 2]A$.

Figure 4, curve *A*, shows this calculated yield with $Z_0 = 29$ for 22 Mev as is observed.⁷ This curve has been made coincident with the extrapolated yield at $Z = 90$ assuming that all of the thorium resonance curve is below 22 Mev. One sees that at $Z = 29$, for copper, the calculated yield is 1.75 times the observed yield. This is approximately what is expected if half of the resonance curve for copper exceeds the upper limit of the bremsstrahlung spectrum. Thus to the rough approximation of these estimates the Goldhaber-Teller theory is in

agreement with the observed yield. Levinger and Bethe⁸ find $\int \sigma dE \propto ZN/A$. This gives approximately the same curve *A*.

It has not been possible to fit the yield curve by assuming Breit-Wigner resonance curves of widths 0 to 8 Mev and by assuming the threshold energy to be one-half of the resonance energy. The integrated cross section was kept proportional to *A*. The results follow the narrow resonance curve except in the vicinity $Z = 29$. Although the energy dependence of our neutron detector is not tested, it ought to be similar to the dependence for the "long counter."⁹

The ratio of yield for 18 Mev to the yield for 22 Mev, Fig. 6, shows that the resonance curves must have gradually varying shapes as a function of *Z*, because (above $Z = 20$) the ratio changes slowly with atomic number. Below $Z = 20$ the yields, and consequently the ratio of yields is strongly influenced by high thresholds.

Nickel yields for 18 Mev and for 22-Mev bremsstrahlung are each about 45 percent of the general trend. Chemical analysis shows 98.45 percent Ni, 0.86 percent Fe and traces of Sn and Sb. Thus impurities cannot be responsible for the low yields. The fact that the ratio for nickel (Fig. 6) is nearly the same as the ratio for neighboring elements suggests that the shape of the cross-section curve is not radically different for nickel, but it is possible to have a normal ratio with low yields as a result of high neutron binding energy and unusually large (γ, γ) or (γ, p) competition. It would be valuable to know the thresholds and the shapes of cross-section curves for nickel.

⁸ J. S. Levinger and H. A. Bethe, Phys. Rev. **77**, 756 (1950).

⁹ A. O. Hanson and J. L. McKibben, Phys. Rev. **72**, 673 (1947).

Correlation of Geiger Counter and Hall Effect Measurements in Alloys Containing Germanium and Radioactive Antimony 124

G. L. PEARSON, J. D. STRUTHERS, AND H. C. THEUERER
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received November 7, 1949)

The distribution of the solute atoms in ingots of germanium antimony alloys which were prepared according to a prescribed cooling cycle have been measured. The solute was Sb¹²⁴ and its distribution was measured with a Geiger counter. In addition, Hall measurements were made which show that in the impurity saturation range each antimony atom contributes one conduction electron. This makes it possible to determine the solute distribution in non-radioactive samples by the Hall method.

I. INTRODUCTION

THE electric properties of germanium containing small amounts of antimony depend on the concentration of antimony present. In preparing the ingots they are slowly cooled to control the antimony separation which occurs on solidifying a binary alloy. Because of the small concentrations of the antimony, 10^{-2} to

10^{-6} percent by weight, it is impossible to determine quantitatively its distribution in the ingot by ordinary chemical or spectrochemical methods. The availability of a radioactive isotope of antimony (Sb¹²⁴) offers a solution to this problem.¹

¹ A preliminary account of this work was presented by the authors at the American Physical Society meeting in Chicago (November, 1948); Phys. Rev. **75**, 344 (1949).

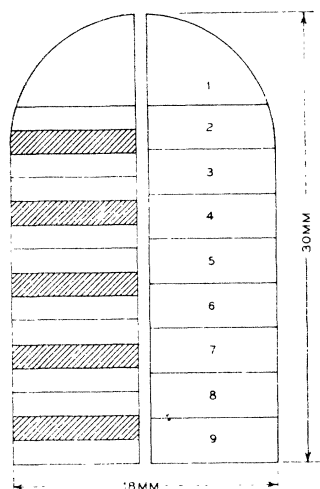


FIG. 1. Dimensions of germanium antimony ingots and method of cutting samples.

It is possible to determine the density of conduction electrons in semiconducting alloys such as these by means of the Hall effect. At low temperatures very few of the impurity antimony atoms are ionized and the density of conduction electrons is low. Raising the temperature increases the ionization and the density until a saturation value is reached around room temperature. A further increase in temperature has no effect on the electron density until one approaches the intrinsic range after which there is a rapid increase due to germanium atom ionization. Our measurements show that in the saturation range the antimony atom density is equal to the conduction electron density. We conclude that in this saturation range every antimony atom is ionized and each atom contributes one conduction electron.² Accurate quantitative analyses can therefore be made on germanium containing extremely small concentrations of antimony by either method.

II. PREPARATION OF SAMPLES³

The source of the germanium used in this study was germanium dioxide obtained from the Eagle-Pitcher Company, Joplin, Missouri. Reduction to the element was accomplished by heating in hydrogen. The Sb^{124} was obtained from the Isotopes Division, AEC, Oak Ridge, Tennessee, and was prepared by irradiating 0.2 gram of antimony metal in the pile. Such treatment gives a product containing approximately 4 millicuries of Sb^{124} having a half-life of 60 days and 55 millicuries of Sb^{122} having a half-life of 2.8 days. The irradiated material was stored for several weeks before using to

² A similar conclusion has been drawn regarding silicon-boron and silicon-phosphorus alloys, G. L. Pearson and J. Bardeen, *Phys. Rev.* **75**, 865 (1949).

³ For a more detailed description of the preparation of germanium ingots see J. H. Scaff and H. C. Theuerer, "Preparation of high back voltage germanium rectifiers," N.D.R.C. 14-555 (October 24, 1945).

allow the Sb^{122} activity to become relatively weak. Sb^{124} decays by two beta-ray emissions having energies of 0.53 and 2.25 Mev respectively, the low energy beta-emission is followed by the emission of a 1.72-Mev gamma-ray. The concentration of Sb^{124} present in the irradiated material as received from Oak Ridge was approximately one part per million with respect to the stable isotopes Sb^{121} and Sb^{123} .

Figure 1 shows the details of the preparation of the samples. A 50-gram charge of germanium, coarsely powdered, was thoroughly mixed with a given weight of powdered antimony (100 percent irradiated antimony for the more dilute alloys and irradiated anti-

TABLE I. Radioactive counts on top surface of slabs cut from germanium ingot H-308 to which 0.0086 percent antimony had been added.

Slab No.	Counts/minute
1	59,000
2	308
3	106
4	80
5	70
6	67
7	64
8	59
9	60

mony plus non-radioactive antimony for the more concentrated alloys). This charge was placed in a graphite crucible having an internal diameter of 18 mm and heated by an induction furnace in an atmosphere of helium. The furnace temperature was raised above the melting point of germanium and allowed to remain for 15 minutes after which the ingot was solidified by slowly raising the induction coil with the power applied. As a result solidification started at the bottom of the ingot and proceeded slowly upward, the total time of solidification being about 30 minutes. Since germanium expands on solidification a round dome was formed at the top. Melts containing 0.00078, 0.0081, 0.0086, and

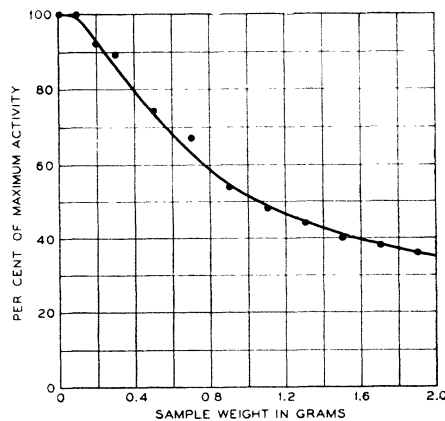


FIG. 2. Self-absorption correction for Sb^{124} in germanium antimony alloys.

TABLE II. Distribution of antimony in germanium antimony alloy ingots.

Slab No.	7.8 × 10 ⁻⁴ % Sb added 2.09 × 10 ¹⁷ Sb atoms/cc			8.1 × 10 ⁻³ %Sb added 2.17 × 10 ¹⁸ Sb atoms/cc			5.39 × 10 ⁻² % Sb added 1.44 × 10 ¹⁹ Sb atoms/cc		
	% Sb	Sb atoms per cc	% Sb added % Sb present	% Sb	Sb atoms per cc	% Sb added % Sb present	% Sb	Sb atoms per cc	% Sb added % Sb present
1	6.18 × 10 ⁻³	1.66 × 10 ¹⁵	7.93	4.58 × 10 ⁻²	1.23 × 10 ¹⁹	5.66	6.56 × 10 ⁻¹	1.76 × 10 ²⁰	12.2
2	6.20 × 10 ⁻⁵	1.66 × 10 ¹⁶	0.0795	5.42 × 10 ⁻⁴	1.45 × 10 ¹⁷	0.0670	1.61 × 10 ⁻²	4.32 × 10 ¹⁸	0.300
3	2.28 × 10 ⁻⁵	6.10 × 10 ¹⁵	0.0292	2.54 × 10 ⁻⁴	6.80 × 10 ¹⁶	0.0314	1.47 × 10 ⁻³	3.94 × 10 ¹⁷	0.0272
4	1.49 × 10 ⁻⁵	3.96 × 10 ¹⁵	0.0192	1.56 × 10 ⁻⁴	4.18 × 10 ¹⁶	0.0193	9.68 × 10 ⁻⁴	2.59 × 10 ¹⁷	0.0180
5	1.21 × 10 ⁻⁵	3.22 × 10 ¹⁵	0.0156	1.15 × 10 ⁻⁴	3.08 × 10 ¹⁶	0.0142	8.63 × 10 ⁻⁴	2.31 × 10 ¹⁷	0.0160
6	7.7 × 10 ⁻⁶	2.06 × 10 ¹⁵	0.0101	8.37 × 10 ⁻⁵	2.24 × 10 ¹⁶	0.0103	5.07 × 10 ⁻⁴	1.36 × 10 ¹⁷	0.00942
7	5.2 × 10 ⁻⁶	1.40 × 10 ¹⁵	0.00666	6.01 × 10 ⁻⁵	1.61 × 10 ¹⁶	0.00745	4.12 × 10 ⁻⁴	1.10 × 10 ¹⁷	0.00765
8	4.6 × 10 ⁻⁶	1.23 × 10 ¹⁵	0.00590	5.79 × 10 ⁻⁵	1.55 × 10 ¹⁶	0.00714	3.39 × 10 ⁻⁴	9.9 × 10 ¹⁶	0.00630
9	8.2 × 10 ⁻⁶	2.20 × 10 ¹⁵	0.0106	1.07 × 10 ⁻⁴	2.89 × 10 ¹⁶	0.0132	5.05 × 10 ⁻⁴	1.35 × 10 ¹⁷	0.00936

0.054 percent antimony by weight were prepared in this manner. These were designated melts H-309, H-308, H-310 and H-311, respectively. A sample of the antimony used in each ingot was kept for calibrating the subsequent G-M counter measurements.

Each of the ingots was cut in half parallel to its long dimension with a diamond wheel. Nine semicircular slices were cut from right-hand sections and sixteen similar slices were cut from the left-hand sections as shown in Fig. 1.

III. RADIOACTIVITY MEASUREMENTS

A preliminary qualitative determination of the relative antimony distribution in the 0.0086 percent antimony ingot was obtained by the radioautograph technique. For this purpose the flat surface of a half-melt section (previous to slicing) was placed in contact with Ansco No-Screen x-ray film for 5.5 hours. The resulting radioautograph showed that a major portion of the antimony had concentrated near the top of the ingot, that is, in the last material to solidify. There was also indication of a slight concentration of antimony over the entire surface, particularly on the bottom surface of the ingot.

Additional data on the relative distribution of the antimony in the 0.0086 percent antimony ingot were obtained by making radioactive counts on each of the nine semicircular slabs after they had been cut as shown on the right of Fig. 1. Table I gives the number of counts per minute on each slab with the upper surface facing the G-M tube. It can be seen that more than 98 percent of the antimony is in the top section and that there is a marked decrease with depth. In the slabs nearest the top of the ingot there was a considerable difference in the count, and hence in the antimony concentration, from the top and bottom surfaces. For example, slab number 2 gave 308 counts per minute from the top surface and 163 counts per minute from the bottom surface. Slab number 9 gave 60 counts per minute from the top and 100 counts per minute from the bottom, thus substantiating the evidence obtained from the radioautograph that the antimony content tended to be higher at the surface than within the ingot.

It should be emphasized that these results give the relative distribution of antimony in the ingot. In order to obtain quantitative data on the antimony content at any given position in the ingot it was necessary to work out a technique for correlating the counts per minute with the antimony concentration. The method used was to powder the slab under analysis, make a radioactive count on a weighed quantity of the powder which had been placed in a small counting dish, and compare this count with that taken under similar conditions on a weighed amount of the 100 percent antimony sample which had been set aside when the ingot was prepared. All samples were ground to pass a 100 mesh screen, and glass counting dishes of uniform diameter were used.

The above counting method automatically corrects for the decrease in radioactivity with time. The sample size taken, however, was sufficiently large in most cases to make it necessary to correct for the absorption of the beta-particles by the germanium present. To determine this correction 2.5 grams of germanium, powdered to pass a 100-mesh screen, was thoroughly mixed with 2.5 ml of standard Sb¹²⁴ solution. This solution was prepared by dissolving 1.126 mg of Sb¹²⁴ in a small amount of *aqua regia* and diluting to 100 ml with water in a volumetric flask. 0.1 ml, equivalent to 1.126 μg of

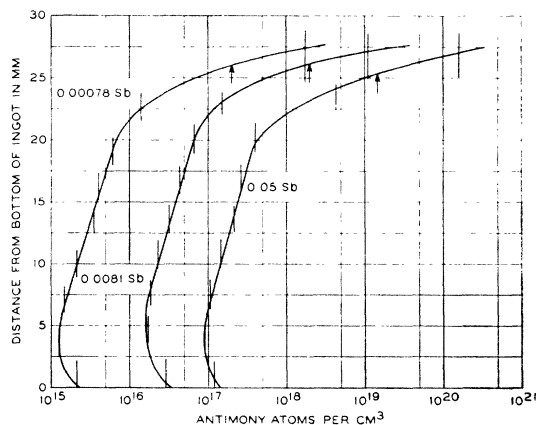


FIG. 3. Distribution of antimony atoms in ingots of germanium antimony alloy ingots.

antimony, gave approximately 600 counts per minute. This mixture was then dried and thoroughly mixed by grinding in an agate mortar. Counts were made on weighed amounts of the mixture from 0.3 to 2.0 grams. The percent maximum activity per unit weight of sample, in this case 0.1 gram is given by the following:

Percent maximum activity

$$= \frac{\text{sample count} \times 0.1 \text{ gram} / (\text{sample wt.} \times 100)}{\text{zero weight count}}$$

The zero weight count is obtained by counting 0.1 ml of the standard Sb^{124} solution, under the same conditions as the sample; this being equivalent to the amount of antimony present in 0.1 gram of sample. Plotting the

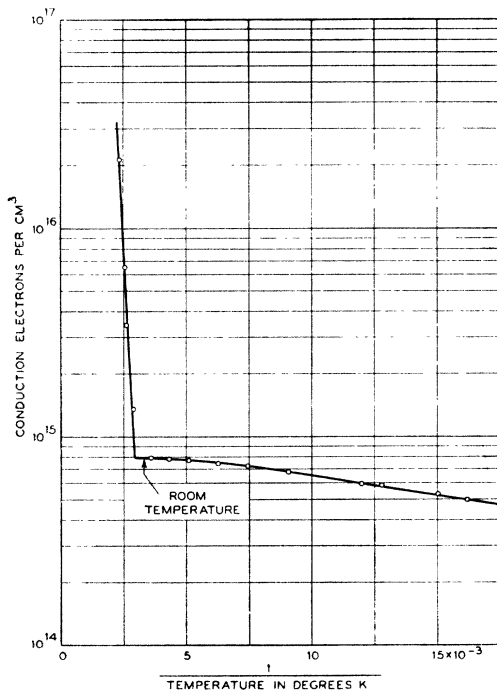


FIG. 4. Conduction electrons in a high purity germanium sample versus the reciprocal of the absolute temperature.

percent maximum activity against sample weight gives the self-absorption curve shown in Fig. 2.

A summary of the data obtained on three ingots in the manner described is given in Table II. The results for each of the nine slices in each ingot are given in terms of: (1) The weight percent of the antimony, (2) the number of antimony atoms per cm^3 , and (3) the ratio of the antimony added to the melt to the amount present. The number of antimony atoms per cm^3 as a function of the distance from the bottom of the melt is plotted in Fig. 3. The length of the experimental lines in this figure indicate the width of the slice before powdering. The arrows show the average concentration of solute atoms which were placed in the charge before melting. Notice that the concentrations in the dome

slices are about 10 times the amount added, whereas the concentrations in the lower half of the ingot are less than one percent of this amount. The observed changes in antimony concentration with location in the ingot are to be expected from the basic nature of the freezing process. When a germanium antimony alloy freezes over a range of temperatures, the first material to solidify contains less antimony than the last material to freeze. This effect is known as coring and the resulting concentration differences persist in the solid material unless they are eliminated by diffusion.⁴ Coring normally manifests itself as a gradient in concentration between the center and periphery of dendritic grains, but in this case since the growth process is from the bottom of the ingot upward the differences in concentration occur gradually from bottom to top in the ingot. Microscopic examination reveals the presence of second phase material at the extreme tips of these ingots which suggests that for these locations the concentrations of antimony were above the solid solubility limit.

IV. HALL MEASUREMENTS

In a semiconductor such as germanium the number of conduction electrons per unit volume can be obtained from Hall effect measurements. In the low temperature or impurity range where the charge carriers arise solely from the impurity centers, the antimony atoms in the present study, the relation is

$$n = \pm (3\pi/8eR) = \pm 7.4 \times 10^{18}/R, \quad (1)$$

where n is the number of charge carriers per cc and R is the Hall coefficient in $\text{cm}^3/\text{coulomb}$. The plus sign applies to p -type impurities which furnish holes and the negative sign to n -type impurities which furnish electrons. Antimony is an n -type impurity and the conduction charges are electrons.

Figure 4 gives conduction electrons per cm^3 versus the reciprocal of the absolute temperature for a typical

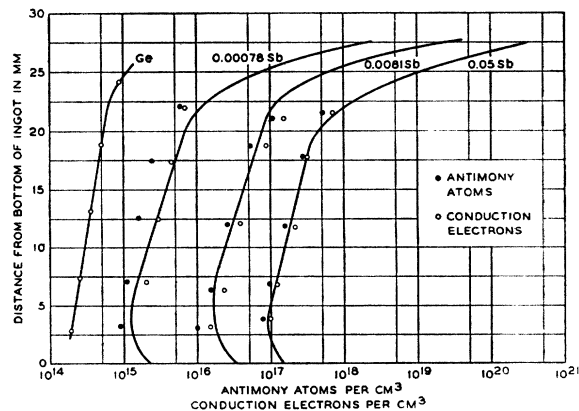


FIG. 5. Correlation of antimony atoms and conduction electrons in germanium antimony ingots at room temperature.

⁴ R. M. Brick, Trans. A.I.M.E. 161, 65 (1945).

high purity *n*-type germanium sample. The straight line portion on the left is the intrinsic range and the portion to the right of the break in the curve is the impurity range. At low temperatures very few of the impurity atoms are thermally ionized and the number of conduction electrons is low. As the temperature is raised ionization increases, thus causing an increase in the number of conduction electrons. Near room temperature a saturation region is attained in which all the impurity atoms become ionized and the number of conduction electrons is constant. It is in this saturation region that we find one conduction electron for each antimony atom as will be shown by comparing the G-M counter and Hall measurements on identical samples.

The left half of the ingots were cut into thin rectangular wafers approximately 0.5 mm in thickness. Measurements were made on the cross-hatched samples as shown in Fig. 1. First the density of conduction electrons in the saturation range was determined from Hall measurements, then the wafers were powdered and the density of antimony atoms was determined from radioactive measurements on the identical material. The results are plotted in Fig. 5 as a function of the position in the melt. The open circles represent conduction electrons per cc and the solid circles antimony atoms per cc. The solid lines are reproduced from Fig. 3 and give the antimony distribution in the other half of the melt as determined from radioactivity measurements. There is a close agreement between the conduction electron and antimony atom densities with the former usually being a little larger.⁵ Within the experimental error these results show that when ionized each impurity atom produces one conduction electron.

Having obtained this result, impurity atom densities can now be determined from Hall measurements alone either on radioactive or non-radioactive samples. As an example, such measurements have been made on a high purity germanium melt to which no impurity had been deliberately added. The results are given by the curve on the left of Fig. 5 which shows about 2×10^{14} donor atoms per cc at the bottom of the melt and 1×10^{15} per cc near the top. It should be pointed out that if both donor and acceptor atoms are present, Hall measurements give only the excess of one over the other. As a method of quantitative analysis, Hall measurements are very sensitive. Since there are 4.5×10^{22} germanium atoms per cc, impurities present to only one part in two hundred million have been detected.

⁵ Recent measurements by J. R. Haynes (private communication) using pulse techniques give conduction electron densities 30 percent lower than those determined by Hall measurements and therefore check the impurity atom densities even better.

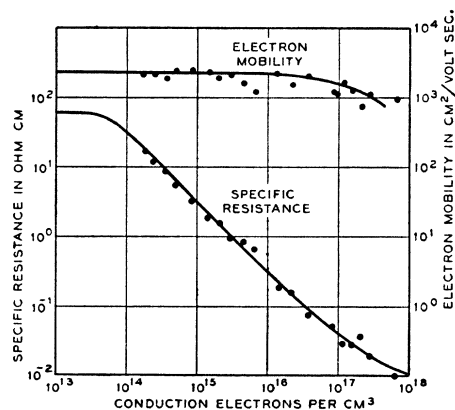


FIG. 6. Specific resistance and electron mobility as a function of electron density in germanium antimony alloys at room temperature.

V. RESISTIVITY AND ELECTRON MOBILITY VERSUS ANTIMONY CONTENT

Electrical resistivity measurements at room temperature were made on the twenty-five rectangular shaped samples which had been prepared for Hall measurements. These are shown in Fig. 6 where specific resistance in ohm cm is plotted *versus* the number of conduction electrons per cc. Over a major portion of the curve the resistivity is inversely proportional to the electron density. The constant value of 60 ohm cm at low impurity content arises from thermally ionized germanium atoms and is obtained by extrapolating the intrinsic resistivity *versus* temperature characteristic to room temperature.⁶

The electron mobility is defined by the fundamental relation

$$\sigma = 1/\rho = ne\mu, \quad (2)$$

where ρ is the specific resistance in ohm cm (σ = conductivity), n is the density of conduction electrons, e ($= 1.6 \times 10^{-19}$ coulomb) is the electronic charge, and μ is the mobility in cm² per volt sec. Mobility has been calculated from the measured values of ρ and n and plotted as a function of n in Fig. 7. It can be seen that μ is constant for values of n up to about 5×10^{16} after which it decreases with further increase in n .⁷ This characteristic is expected from theory² since the constant value is due to scattering by the germanium lattice while the decrease at high impurity concentration arises from the added scattering of the antimony atoms.

The linear relationship between resistivity and the density of conduction electrons at room temperature (equal to the density of antimony atoms) suggests resistivity measurements at room temperature as a simple analytical method for determining the quantity of antimony in germanium alloys.

⁶ G. L. Pearson, Phys. Rev. **76**, 179 (1949).

⁷ Similar curves have been given for germanium copper alloys by W. Ringer and H. Welke, Zeits. f. Naturforschung **1**, 20 (1948).