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THEORETICAL RESISTIVITY AND HALL COEFFICIENT OF IMPURE GERMANIUM NEAR ROOM TEMPERATURE

RADIO CORPORATION OF AMERICA
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Approved

Stuart Wm Seeley

Introduction

The resistivity of high-quality single-crystal germanium is determined by its impurity content and in turn resistivity can be used as a measure of purity. The semiconductor device engineer will find it most convenient to specify germanium purity in electrical terms by its conductivity type (n or p) and its resistivity at some standard temperature such as 25 degrees C. In this bulletin, the temperature variation of resistivity over the range −75 degrees C to +125 degrees C has been calculated and plotted for both p-type and n-type germanium with different impurity content, ranging from 0.1 ohm-cm to 60 ohm-cm at 25 degrees C.

When germanium is first purified and then intentionally doped with an added single impurity, it is desirable to know the relationship between actual impurity content and resistivity and Hall coefficient. Ordinarily, with reasonably perfect crystals, resistivity is sufficient to specify impurity; on the other hand, if crystal perfection is uncertain, the Hall coefficient is a more reliable index. These relationships have been calculated for 25 degrees C and are plotted, again for both n and p-type. The curves can be used either to predict electrical values from known impurity content, or to interpret measured electrical values in terms of germanium analysis.

A useful rule of thumb that applies between 20 ohm-cm and 0.1 ohm-cm at 25 degrees C (the resistivity range useful for transistors) gives the inverse proportionality between impurity content and resistivity, ρ (in ohm-centimeters), as follows:

$$\text{mol-fraction of impurity} = \frac{3.8 \times 10^{-8}}{\rho} \qquad \text{(for n-type germanium)}$$

$$\text{mol-fraction of impurity} = \frac{8.1 \times 10^{-8}}{\rho} \qquad \text{(for p-type germanium)}$$

In the past, it has sometimes been expedient with higher resistivity materials to assume that the conductivity of germanium is equal to a constant intrinsic part plus the conductivity imparted by one electron (or hole) per impurity atom. The error in this assumption has been investigated and graphs of the approximate and exact values are compared.

General Discussion

The heart of a germanium device is the germanium from which it is made. The performance of the ultimate rectifier or transistor will depend greatly on the electrical characteristics of the starting semiconductor material. This bulletin is concerned only with germanium, although other semiconductors can be treated in a similar manner.

The electrical behavior of bulk germanium is determined largely by two factors, crystal perfection and impurity content. Techniques are well developed[1] for growing single crystals that exceed the perfection required in transistors and the theory and practice of x-ray determination of the crystal structure has already been described[2]. The second factor, impurity content, is measured in terms of very small fractions, about one part in one hundred million, for interest in the transistor field. Such small impurity concentrations are beyond the detection range of conventional chemical or physical analysis. However, because these small concentrations determine the interesting electrical behavior of the germanium, the electrical measurements of resistivity and Hall coefficient can, in turn, be used to evaluate the impurity content of the material. Indeed, it has become quite customary to specify the purity of germanium by its resistivity. The technique of the electrical measurements has been described in another bulletin[3]. The present work is a computation and graphical plot to assist in the interpretation and utilization of measured resistivity and Hall-coefficient values as well as in predicting the electrical effects to be expected at various temperatures from a given impurity concentration.

Since the Hall-coefficient is a direct and unique measure of the electrical carrier concentration (and hence the impurity content) in germanium below about 20 ohm-cm in resistivity, it is the most reliable measure of purity, especially when the crystal perfection is uncertain. In cases, however, where a high-quality single-crystal is under consideration, resistivity will furnish an adequate evaluation of the material. Since it is a simpler measurement to make, resistivity will normally be the criterion used by the engineer to evaluate germanium.

For the device engineer, the most important part of this study will be the information on the temperature dependence of resistivity of germanium. This provides the basis for understanding how certain important device parameters (e.g., equivalent base resistance of a transistor) vary with temperature. Another important matter which will be clarified is that n-type and p-type germanium of a given resistivity at room temperature may not exhibit the same temperature variation.

For the scientist charged with purifying germanium and re-constituting its impurity content ("doping"), this bulletin will aid in converting room-temperature resistivity and Hall-coefficient measurements to absolute and relative impurity concentrations and vice versa. It is of interest that n-type and p-type germanium of the same resistivity correspond to different impurity concentrations. Of even greater significance is the fact that with increasing purity, the curve of approach to a limiting (intrinsic) resistivity is entirely different for the two conductivity types.

The basic equations used in this study, and the necessary physical constants of germanium are all conveniently available in a single reference[4]. The novelty in the present work lies in (a) modifying the $T^{3/2}$ dependence of mobility to agree with recent experiments performed at RCA Laboratories, (b) solving the necessary equations simultaneously to get the quantities desired, and (c) plotting numerical values in the range of interest.

The curves given cover the temperature range of -75 degrees C to +125 degrees C, and the resistivity range from 0.1 ohm-cm at 25 degrees C to intrinsic or pure germanium (6[illegible] ohm-cm at 25 degrees C). The temperature 25 degrees C (77°F) is emphasized as being representative of the room temperature at which measurements are often made.

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[1] LB-892 *Preparation of Single Crystals of Germanium and Silicon.*

[2] LB-881 Determination *of Orientation and Deformation of Germanium Crystals.*

[3] LB-885 *Electrical Measurements on Germanium.*

[4] W. Shockley, ELECTRONS AND HOLES IN SEMICONDUCTORS, Van Nostrand, N.Y. 1950.

Basis of Calculations

A physical picture of conduction in semiconductors may be found in Shockley's book[4] and has also been given in another bulletin[5]. The application of theory is based on the following assumptions:

1. Only a single impurity type is present.
2. Each significant impurity atom contributes one energy state in the forbidden energy band[6].

These assumptions do not seriously curtail the applicability of the results provided that: (a) The material is first purified and then doped with a single impurity as is the current practice for germanium devices. (b) The significant impurity is from column three (for p-type) or five (for n-type) of the periodic table, which is also common practice in doping. Even when the impurities arise from partial purification without redoping, these results may still be used as an approximate guide to the "net" impurity concentration -- that is, the difference in the concentrations of n-type and p-type impurities. In this case, as well as when doping has resulted in more than one significant impurity being present, an extension of the resistivity measurements to liquid helium temperatures will furnish a better analysis as discussed in the other bulletin[5].

Theory

Complete details of the calculations will not be described but a brief outline of the physical and mathematical bases for the computations will be given here.

The resistivity ρ (or its reciprocal, the conductivity σ) depends only on the electronic charge q (a positive constant), and the concentrations and mobilities of the electrons and holes (n, μ_n, p, μ_p, respectively) that are the electrical carriers in the conduction process. The equation is

$$\sigma = 1/\rho = q(n\mu_n + p\mu_p) \quad (1)$$

The mobilities are constants of the germanium, the electron mobility being about twice that for holes. In the range of interest, the mobilities are determined by lattice scattering and are slowly varying functions of the absolute temperature, T. This dependence has generally been assumed to be a proportionality to $T^{-3/2}$. Recent studies made at RCA Laboratories have revised this dependence and the following variation is assumed here:

$$\mu_n = 3600\ (298/T)^2\ \text{cm}^2/\text{volt-sec} \quad (2)$$

$$\mu_p = 1700\ (298/T)^2\ \text{cm}^2/\text{volt-sec} \quad (3)$$

The electron and hole concentrations are further related by an equation expressing the electrical neutrality of the material:

$$n + n_d + N_a = p + p_a + N_d \quad (4)$$

where N_d and N_a are concentrations of total donor and acceptor impurity atoms and n_d and p_a are concentrations of un-ionized donor and acceptor atoms.

The following simple expressions can now be written relating the various concentrations with the temperature and with universal constants. The Fermi level E_F appears implicitly in these relations, but need not be solved for explicitly. It has been determined and plotted, however, since other questions can be answered directly by a knowledge of its behavior.

$$n = CT^{3/2} \exp\ (E_F - E_c) \quad (5)$$

$$p = CT^{3/2} \exp\ (E_v - E_F) \quad (6)$$

$$n_d = N_d \exp\ (E_F - E_d) \quad (7)$$

$$p_a = N_a \exp\ (E_a - E_F) \quad (8)$$

The E_x's are dimensionless; that is, energies are expressed in units of kT. Only energy differences are involved. E_c is the floor of the conduction band; E_v is the roof of the valence band; E_d is the donor level and E_a is the acceptor level. The equations are all simplifications of Fermi distributions which hold true because the Fermi level is at least several units of kT away from any of the other energy

[5] LB-886 *Low-Temperature Electrical Measurements on Semi-Conductors.*

[6] This has been proved experimentally for antimony by G.L. Pearson, J.D. Struthers, and H.C. Theurer, "Correlation of Geiger Counter and Hall Effect Measurements", *Physical Review*, vol. 77, pp. 809-813 (March 15, 1950)

levels in the ranges under investigation. C is a theoretical constant which should be compatible with the accepted experimental value of $\rho = 60$ ohm-cm for pure germanium at "room temperature". This "determines" room temperature to be 298 degrees K (25°C).

Also required for a solution are the following values which are known experimentally:

$$(E_c - E_v)\ kT = 0.72 \text{ e.v.} \qquad (9)$$

$$(E_c - E_d)\ kT = 0.1 \text{ e.v.} \qquad (10)$$

$$(E_a - E_v)\ kT = 0.1 \text{ e.v.} \qquad (11)$$

The Hall coefficient is determined from the equation:

$$R = \frac{3\pi}{8} \frac{n\mu_n^{\ 2} - p\mu_p^{\ 2}}{q\ (n\mu_n + p\mu_p)^2} \qquad (12)$$

Results

Fig. 1 gives the resistivity of n-type germanium as a function of temperature. The running parameter is the resistivity at 25 degrees C (room temperature). This is a useful designation since it corresponds to the conventional specification of purity by the equivalent resistivity. Later graphs provide a transformation to absolute expressions of purity. Note that for 16 ohm-cm and below, the resistivity has a positive temperature coefficient at room temperature (because of the mobility variation). At sufficiently high temperatures, however, a sample of any given purity will assymptotically approach the intrinsic curve which has the negative slope characteristic of an intrinsic semiconductor.

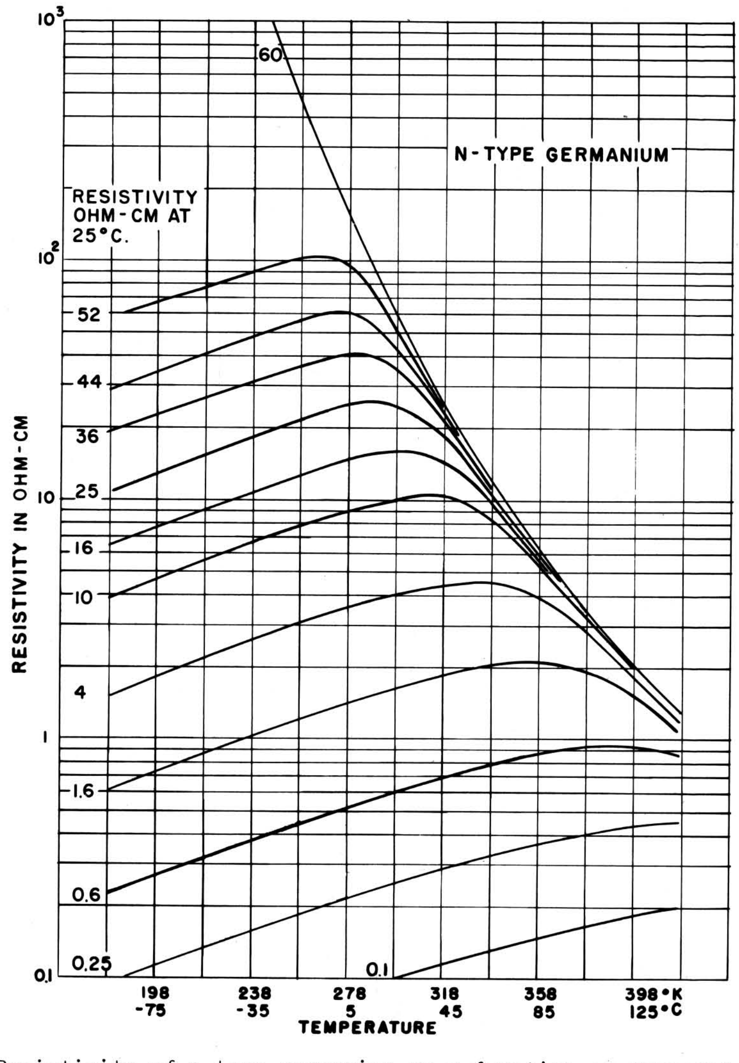

Fig. 1 – Resistivity of n-type germanium as a function of temperature.

Fig. 2 gives a similar family of curves for p-type germanium. It is seen that the curves cross the intrinsic (60 ohm-cm) curve and approach it assymptotically from the high resistivity side. This effect is explained as follows: When p-type impurity is added to pure germanium, the concentration of holes increases and the concentration of electrons decreases. Since the holes have the lesser mobility, this adds more to the resistivity at first than it takes away. Ultimately the increase in hole concentration with impurity addition is the only significant effect and the resistivity decreases as with n-type germanium. The maximum resistivity reached at room temperature is 64 ohm-cm. Room temperature resistivities between 60 and 64 cannot be uniquely interpreted in terms of impurity content, but practically speaking this is a very limited region and results in no handicap.

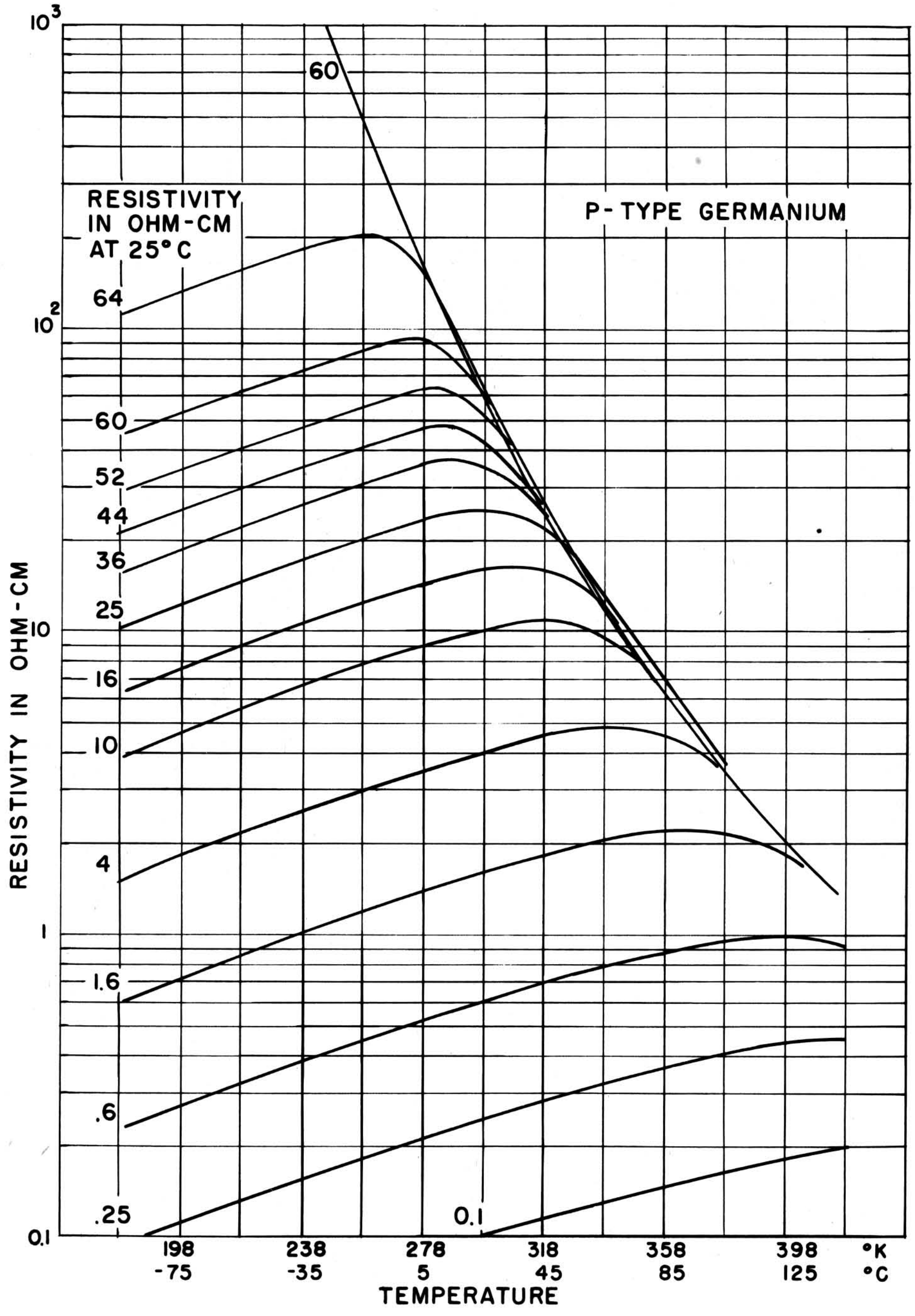

Fig.2 - Resistivity of p-type germanium as a function of temperature.

Fig. 3 is an enlarged view of curves taken from Figs. 1 and 2 and shows the different temperature behavior of 52 ohm-cm germanium when it is either p or n-type. It emphasizes that n-type material of a given resistivity is purer than p-type. It is also indicated that the p-type curves are tangent to an envelope marked ρ max. This curve lies 4 ohm-cm above the intrinsic curve at room temperature.

Fig. 4 is an enlargement of other curves from Figs. 1 and 2, and shows that for le pure material the p and n curves coincide below room temperature. One should bear in mind, however, that using room-temperature resistivity as a parameter to designate purity is somewhat artificial and that the ratio of impurity content in the p and n curves of Fig. 4 is not the same as in the p and n curves of Fig. 3.

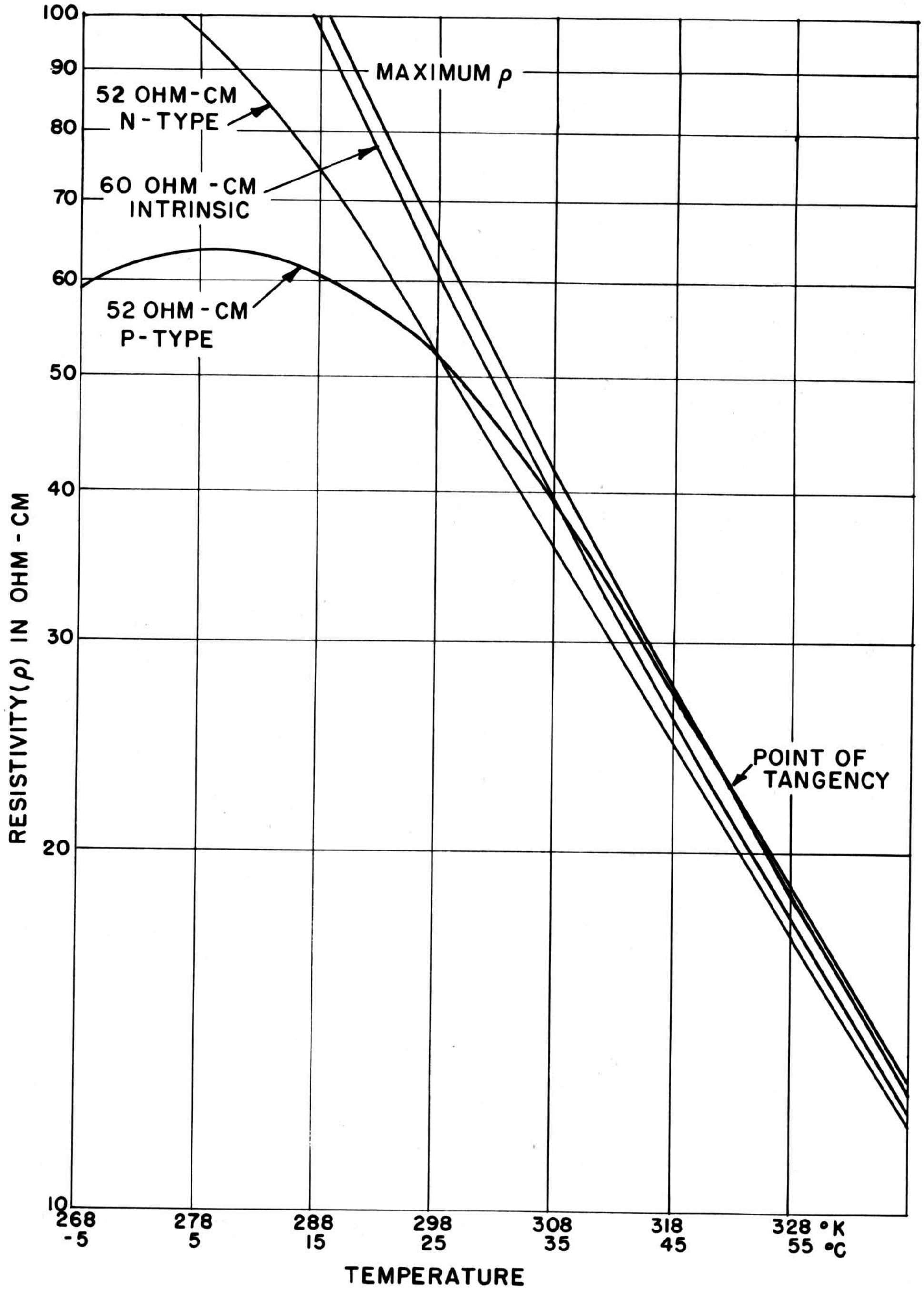

Fig.3 – Comparison of 52 ohm-cm germanium, both n and p-type.

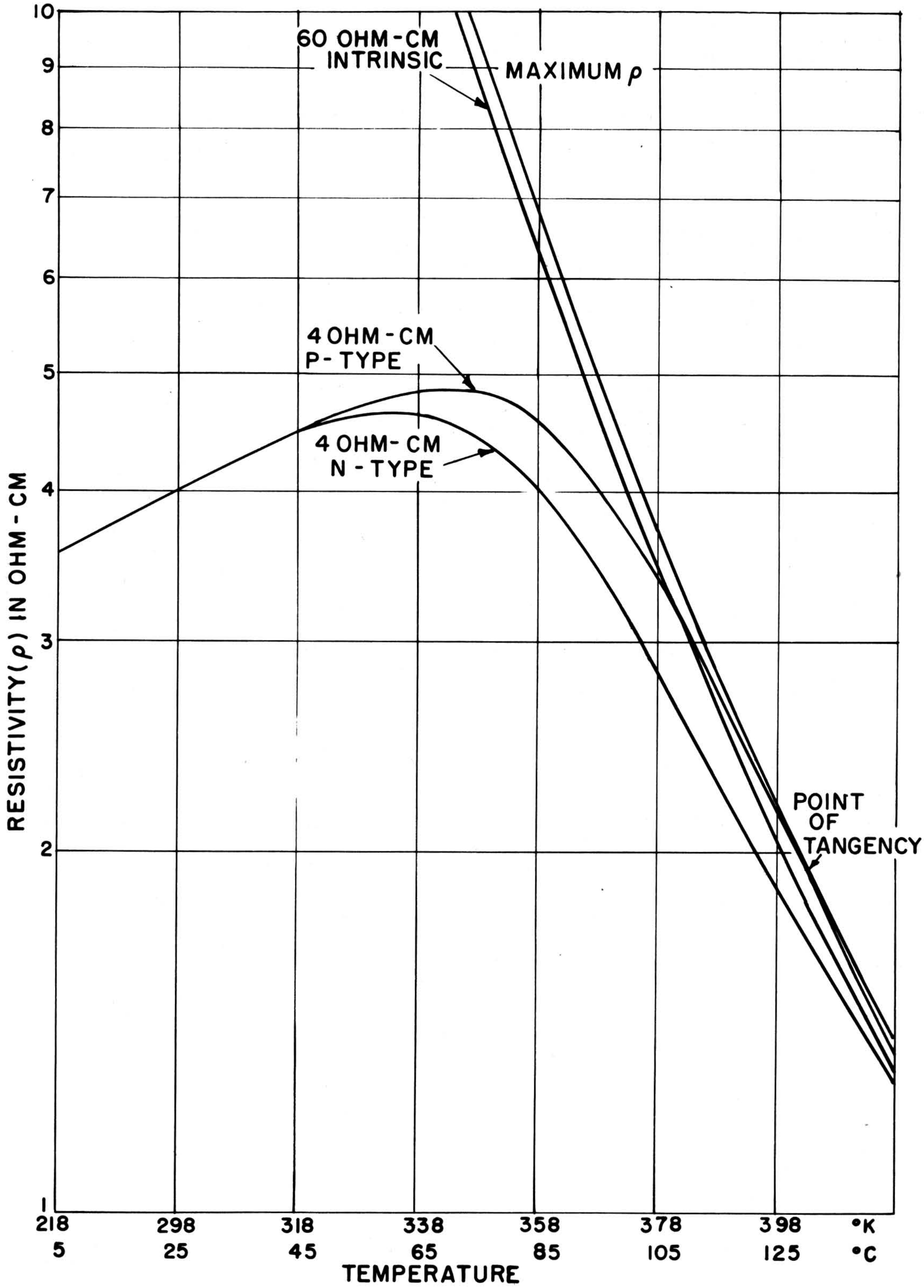

Fig.4 – Comparison of 4 ohm-cm germanium, both n and p-type.

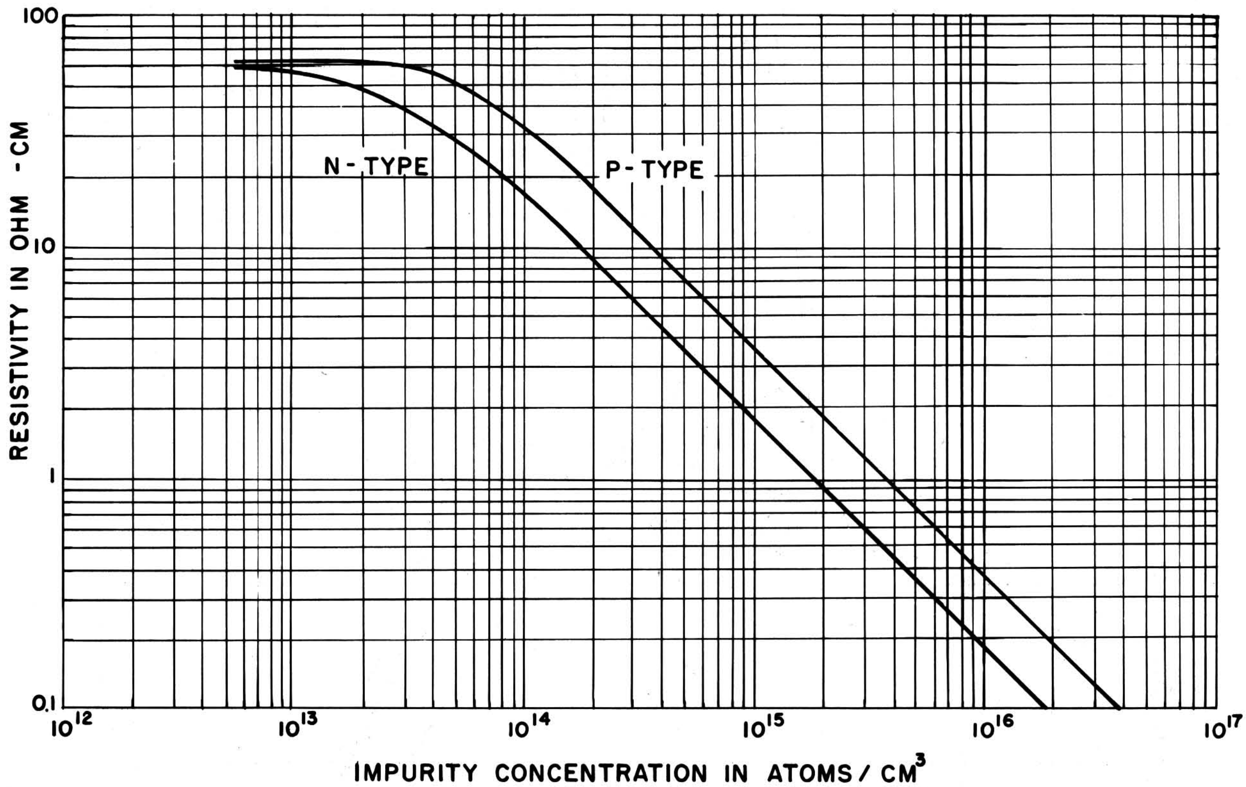

Fig.5 – Resistivity versus absolute impurity concentration for germanium at 25 degrees C.

Fig. 5 relates the room temperature resistivities used above to absolute impurity concentration in atoms/cm^3. As already stated this implies that each impurity atom contributes one extra energy state near the top or bottom of the forbidden energy band.

Fig. 6 gives the same information as Fig. 5 except that impurity concentration has been expressed as a mol-fraction, that is, the ratio of impurity atoms to germanium atoms. The conversion factor is the atomic density of germanium, 4.55×10^{22} atoms/cm^3. It is seen that the log-log plots are linear for resistivities below about 20 ohm-cm. The resistivity in ohm-cm and the impurity concentration in mol-fraction are then related by these simple equations which are conveniently remembered:

$$N_d = 3.8 \times 10^{-8} / \rho$$

$$N_a = 8.1 \times 10^{-8} / \rho$$

These relations are not accurate below about 0.1 ohm-cm because impurity scattering then begins to affect the mobility.

Fig. 7 contains the information of Fig. 6, but plots conductivity as ordinate. This enables one to see the magnitude of the error made in assuming, as is sometimes done, that the conductivity of a germanium sample may be considered the sum of two contributions: a contribution corresponding to one carrier per impurity atom plus a contribution of 1/60 $(\text{ohm-cm})^{-1}$ of "intrinsic" conduction. This ignores the fact that the addition of electron carriers, for example, reduces the equilibrium concentration of hole carriers. Thus the simplified picture of conductivity just described predicts too high a value as shown by the dashed curve.

Fig. 8 gives the Hall coefficient. For n-type this behaves much like the resistivity of p-type germanium. The reason is that the hole effect subtracts from the electron effect. As the hole contribution vanishes with increasing n-type impurity, it first causes the Hall coefficient to rise before the characteristic of a single type of carrier dominates the picture. The Hall coefficient for p-type

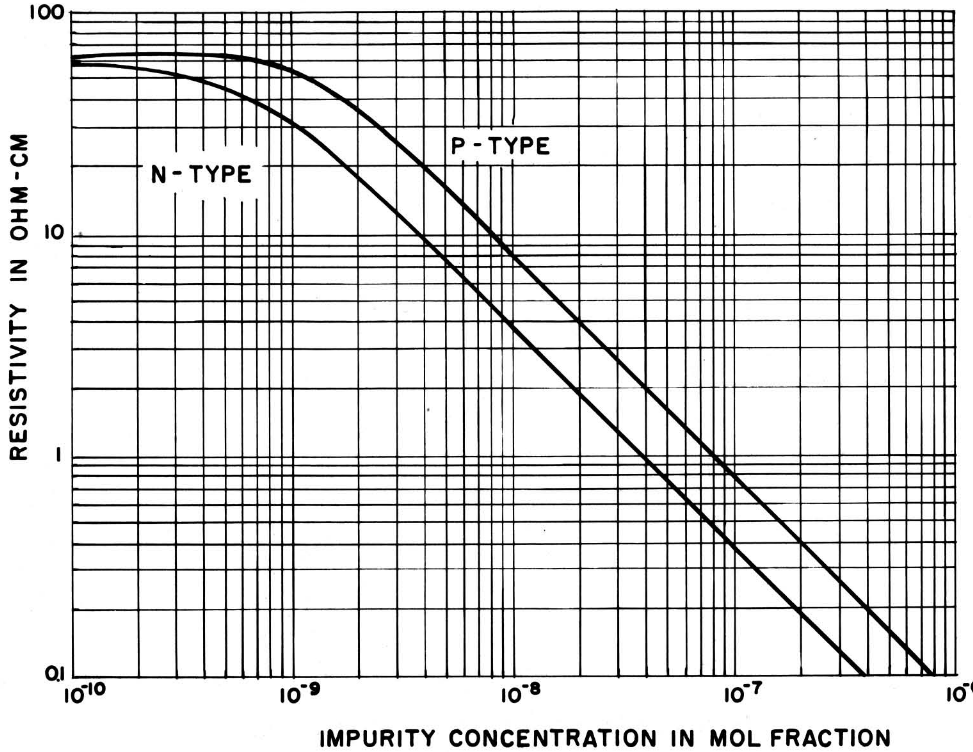

Fig.6 – Resistivity versus relative impurity concentration for germanium at 25 degrees C.

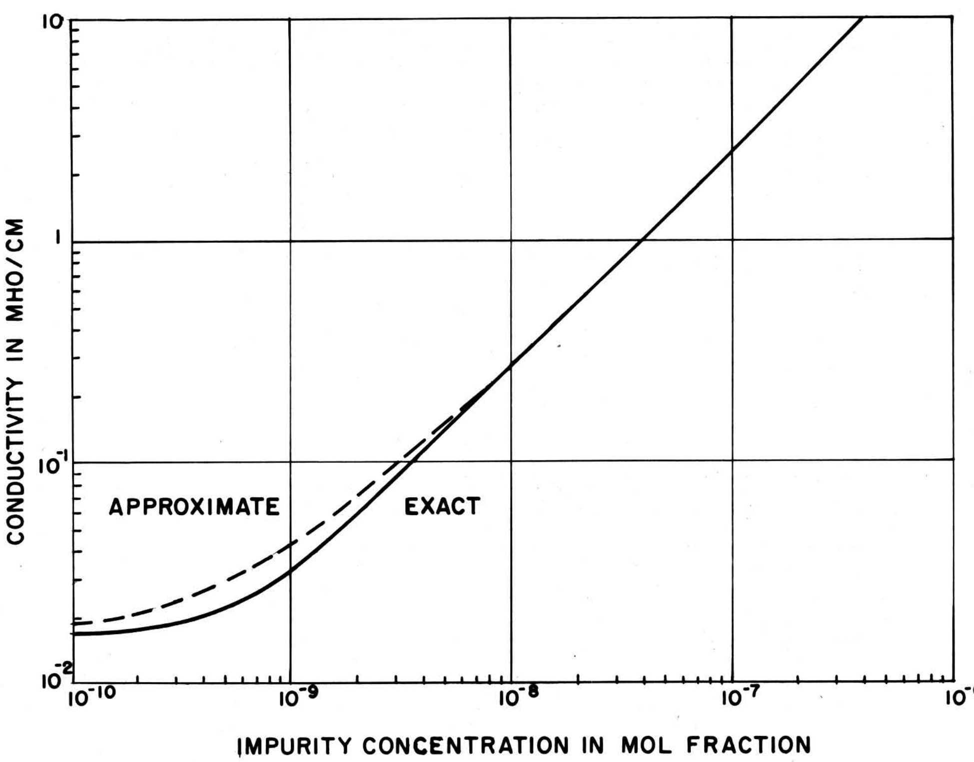

Fig.7 – Conductivity of germanium at 25 degrees C compared with approximate values obtained by adding intrinsic and impurity conductivities independently.

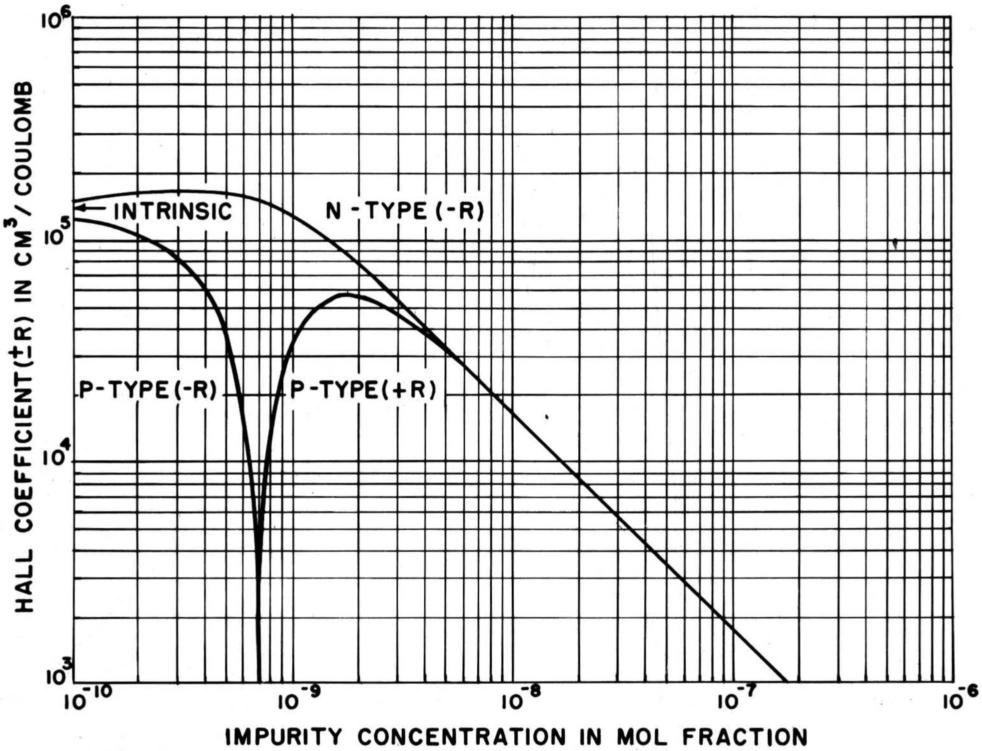

Fig.8 – Hall coefficient versus relative impurity concentration for germanium at 25 degrees C.

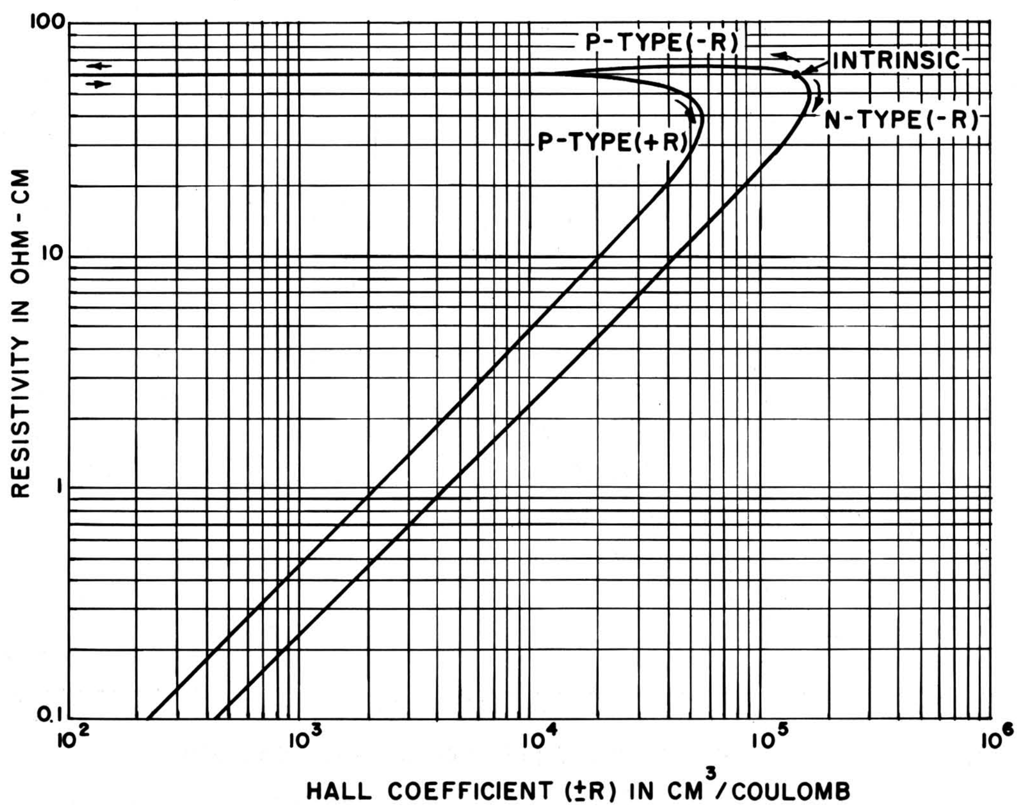

Fig.9 – Resistivity versus Hall coefficient for germanium at 25 degrees C.

germanium goes through zero and changes sign. The reason is that the holes predominate in impure material. With increasing purity, the concentrations of holes and electrons approach equality. Since electrons have the greater mobility, they then preponderate.

Fig. 9 gives the Hall coefficient as a function of resistivity. Since these are the two data generally available after making Hall measurements, the curves are useful in determining whether the actual mobilities match those assumed in the calculation, which represent values for high-quality germanium.

Fig. 10 gives the displacement of the Fermi level from the center of the forbidden band. It is actually applicable to either n-type or p-type although it is drawn as referred to donor impurities. For n-type, energies are measured toward the conduction band; for p-type, toward the valence band.

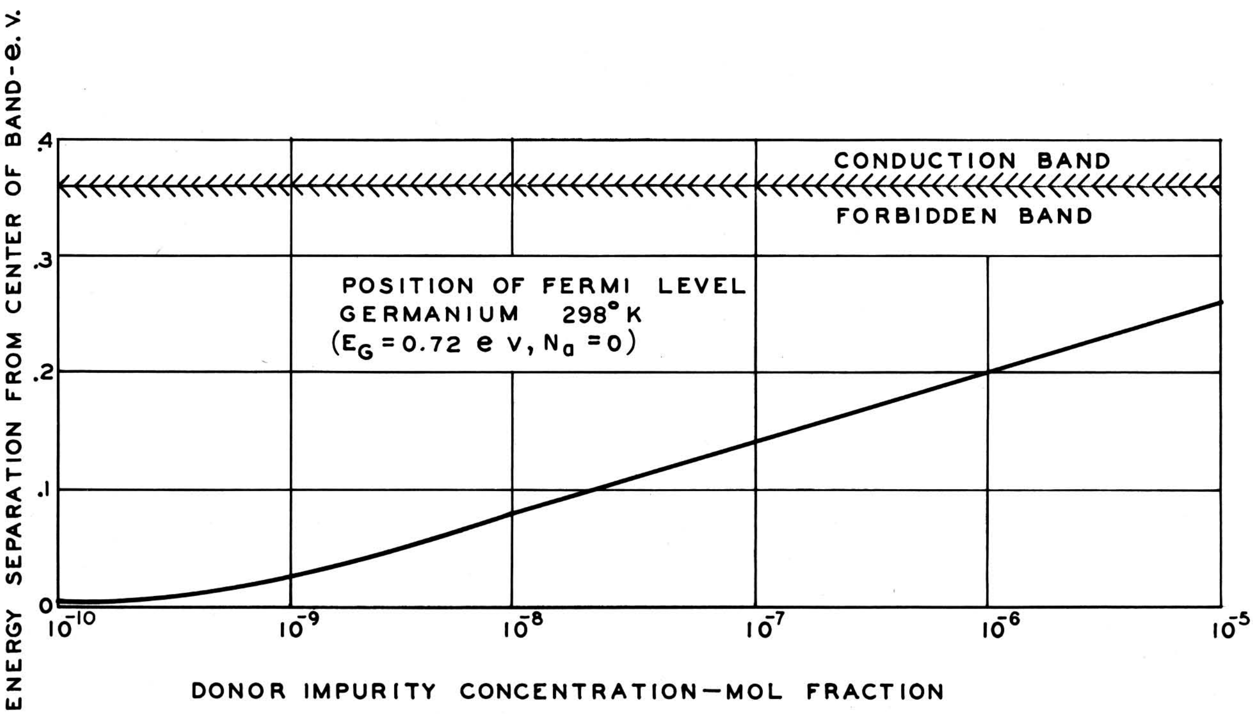

Fig. 10 - Position of Fermi level for germanium at 25 degrees C.

Paul G. Herkart

Jerome Kurshan