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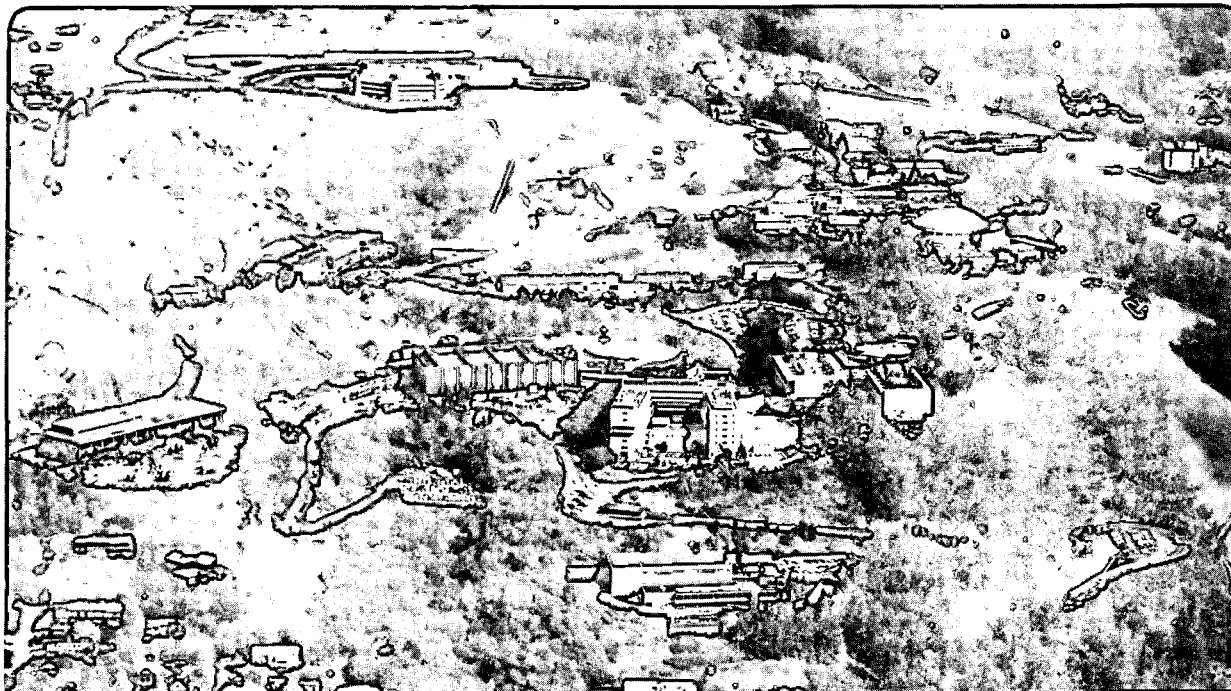
THE PHOTO HALL EFFECT IN BERYLLIUM DOPED GERMANIUM

T.A. Germer
(Sr. Thesis)

May 1985

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THE PHOTO HALL EFFECT IN BERYLLIUM DOPED GERMANIUM

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Senior Thesis

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ABSTRACT

The photo Hall effect was investigated as a characterization technique for multilevel p-type germanium crystals, especially Ge:Be. The free hole concentration is derived as a function of temperature and illumination, and an increase in the free hole lifetime was predicted as a result of a population inversion created by optical pumping and is found to occur, by as much as a factor of 100, when the concentration of shallow acceptors is slightly less than the concentration of donors. The recombination coefficient for the capture of holes by Be^- was found to be $1.3 \times 10^{-5} \text{ cm}^3/\text{sec}$ at 8K and its temperature dependence is approximately $T^{-0.7}$. The apparatus is described in detail, and the theory is explained for the systems discussed. Attempts were made at curve fitting, and problems found are explained.

ACKNOWLEDGEMENTS

I wish to thank Professor Eugene Haller for his resources and guidance in helping me to carry out this research. I would like to thank Professor Leo Falicov for his aid in allowing me to do my work outside the physics department and Professor Howard Shugart for granting me credit for advanced laboratory for the experimental work. I wish to express my thanks to Nancy Haegel, to whom I am indebted for her help and guidance, her research which motivated this work, and her infallible patience. This work was made easier with the aid of Dick Davis, Bill Hansen, and Jeff Beeman. Finally, I would like to express my gratitude towards my other associates for inspiring me in this field and allowing me to work along side them: Bob McMurray, Joe Kahn, Kevin Jones, and David Nolte.

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1. INTRODUCTION

Semiconductors have a number of interesting properties that cannot be explained with classical theories. The fact that a semiconductor has a negative temperature coefficient of resistivity at low temperatures is one example. Another is the strong influence that impurities have on the electrical properties. Impurities with concentrations of one part in 10^{11} will greatly influence the characteristics of the material. In order to explain such phenomena, quantum mechanics is required.

Quantum mechanics explains a number of interesting properties for a particle moving in a perfectly periodic potential field, such as an electron in a crystal. One immediate result is that a free electron in such a potential field passes through the lattice with zero resistivity. As one would guess, this phenomenon is not observed in practice. The reason for this is that a real crystal exhibits a number of effects which destroy the perfect periodicity. Such effects arise from thermal vibrations (phonons), impurities (electrically active and neutral), and higher dimension structural defects such as dislocations. The ideal property, though, is not totally academic since in quantum mechanics small perturbations in a system can be treated rather nicely. The effect of lattice vibrations in a crystal is treated as if each quantum of vibrational energy were a particle of its own, a phonon. Similarly, an impurity can be treated as if it were a free atom in space, except that it is immobile.

In semiconductors, the optical properties are greatly influenced by certain impurities in the material. For example, one very important contribution to the absorption of photons by a crystal is the absorption by donor or acceptor impurities, either exciting the impurity electron to a bound excited state or by ionizing it to allow an electron (or the absence of an electron, a hole bound to an acceptor) to wander about the crystal as if it

were free. By measuring the absorption as a function of photon energy, one can easily see transitions between various energy levels that exist in the crystal.

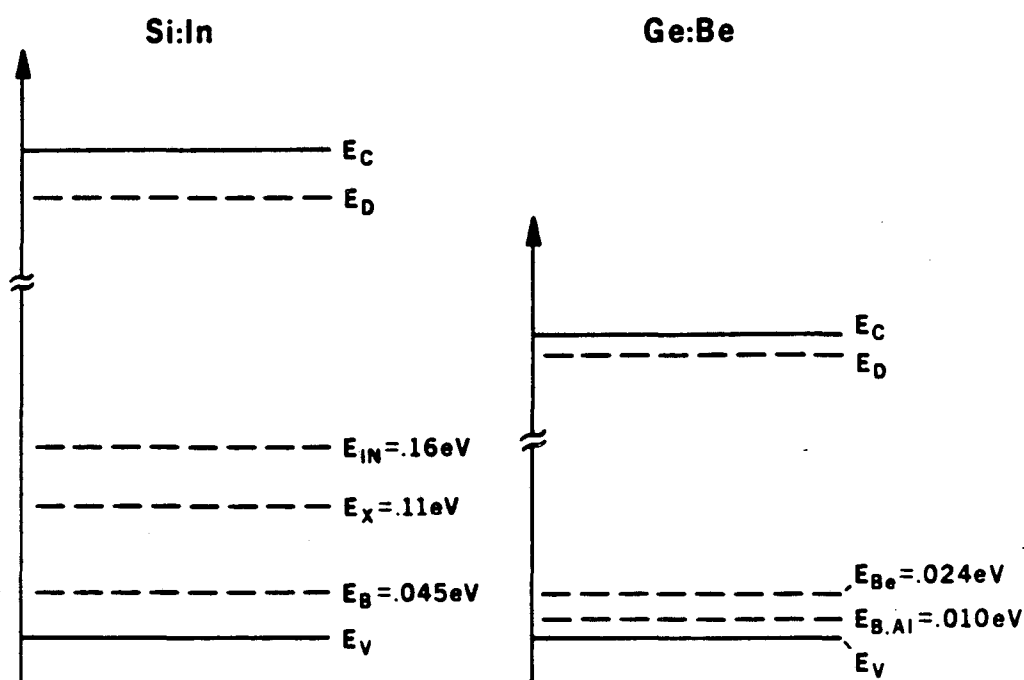
In a pure semiconductor, there exist certain allowed energies that an electron can have and certain forbidden energies an electron cannot have. Those states in which the energies can exist lie in bands which have a range of energies. Likewise, the forbidden energies lie in certain bands called bandgaps. Semiconductors have their unusual properties because the number of electrons in the system is just enough to fill all the states in a band up to a bandgap edge at absolute zero temperature. The next band above the gap is completely empty. These two bands are usually called the valence band and the conduction band respectively, since the electrons in the valence band, when the band is filled, are immobile and the electrons in the conduction band lead generally to conductivity.

In the materials discussed here, it must be understood that an unfilled state in the valence band can also lead to conduction, and we consider the conduction to be due to positively charged holes. These holes are considered to have an energy scale pointing in the opposite direction of the electron energy; thus, a hole with more energy is lower on an energy level diagram (see figure 1).

Let us examine the effect of impurities. Suppose we were to replace one of the germanium atoms with an arsenic atom, which has one extra electron. Since only four of its outer electrons are needed to bond with the other germanium atoms around it, the extra electron does not form a bond with neighboring atoms. When the fifth electron leaves the arsenic ion it leaves behind a positive charge, and it will be attracted to it by the Coulomb field. It is not hard to imagine that the electron will be bound to the impurity arsenic atom by Coulombic attraction in much the same manner as an

electron is bound to a proton in a hydrogen atom. The electron will have a number of states where it can reside (bound states) and conduction band states where it is totally free. The effective mass theory describes such a donor system in terms of a hydrogen atom embedded in a dielectric medium. In an energy level diagram for shallow levels in germanium, the ground state lies about 10 meV from the conduction band. Such an impurity is generally called a shallow or hydrogenic donor.

A similar situation occurs for a group three impurity such as gallium, except that instead of having an extra electron, it needs an extra electron to complete the covalent bonding in germanium. It can be treated in almost the same way as a donor, except that a hole is created in the valence band instead of an electron in the conduction band. Impurities such as gallium, indium, aluminum, and boron produce shallow acceptors. Beryllium and zinc, since they are in the second group in the periodic table, create two holes and are called double acceptors. Since their ionization energy is generally greater than that for shallow acceptors, but not as large as deep levels with energies



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Fig. 1: Energy level diagrams for Si:In and Ge:Be.

near the center of the bandgap, they are often called semi-deep or helium-like acceptors (see figure 1).

We will make a simplifying assumption in this paper. Since at low temperatures the excited states of an impurity are not populated, just as a hydrogen atom has a much higher probability of being in the ground state than in any excited state, we will only consider the ground state of the impurities. This will simplify many of the calculations that follow.

Once an electron or hole is excited so that it is free, it moves through the lattice until something interacts with it to cause it to lose energy and possibly recombine with another ionized impurity, leaving the latter neutral. A free carrier can interact with impurities, phonons, or defects. If one knows how many impurities there are with which an electron or hole may recombine, then it should be possible to find an average time that the electron or hole is free. Each ionized impurity has a cross section for the capture of free carriers. If a certain number of carriers, g_{opt} , are being generated per unit time, then given this average lifetime, we should have an average number of carriers that are free at any one time given by $p = g_{opt}\tau$, where τ is this lifetime, and p is the free carrier concentration.

1.1 The Hall effect

The free hole concentration can be measured by the Hall effect. A sample is placed in a magnetic field and a current is passed in a direction perpendicular to the field. Because the Lorentz force acting on the charge by the magnetic field points in the direction perpendicular to both the field and the current, a charge displacement is produced which creates an electric field that opposes the Lorentz force in equilibrium (see figure 2). The Hall coefficient or Hall resistance is given by the expression

$$R_H = \frac{E_y}{J_x B_z}. \quad (1)$$

The Hall coefficient R_H can be related to conventionally measured quantities, the voltage V , the current I , and the thickness of the sample, d :

$$R_H = \frac{V d}{I B}. \quad (2)$$

By considering a free electron gas, this quantity can be shown to be related to the free carrier concentration n by (in CGS units)

$$R_H = - \frac{r}{nec}. \quad (3)$$

The factor r , called the Hall scattering factor, is a number on the order of unity which enters if the relaxation time of the carriers is a function of their velocity.¹ It is a slowly varying function of field, direction and temperature but is considered to be unity in the high magnetic field limit ($\mu B \gg 1$, where μ is the mobility, given by $e/\rho n$, and ρ is the resistivity).²

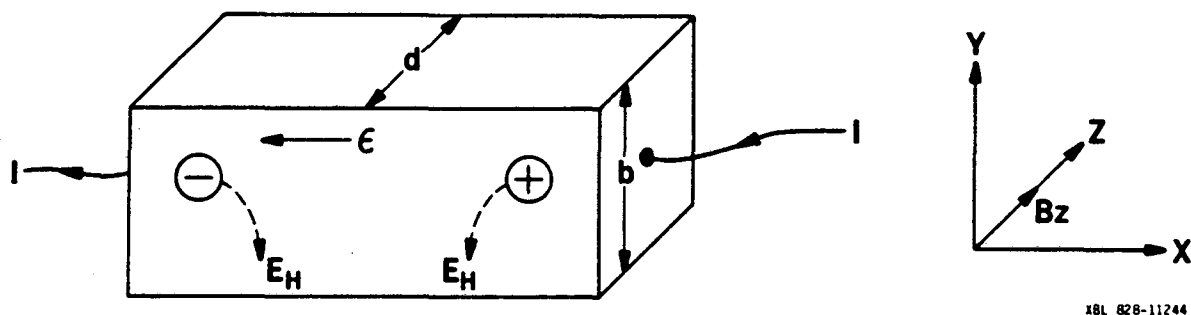


Fig. 2: The effect of electrons and holes in the Hall effect.

An interesting consequence of the Hall effect is that the Hall coefficient is negative for electrons and positive for holes. This effect can be seen in figure 2 by noticing that holes and electrons tend to be forced in the same direction even though, for a given current, they are moving in opposite directions. In fact, the first detection of a positively charged carrier in a solid was made by means of the Hall effect.

1.2 Photoconductors

Photoconductors are devices that convert optical signals into changes in electrical conductivity. Because photons can be used to generate carriers in a semiconductor, semiconductors have many applications as photoconductors. A photoconductor for detection in the far-infrared basically consists of a piece of a doped semiconductor held at very low temperatures. A bias across the semiconductor creates a very small "dark" current. As light shines on the crystal, free carriers are generated, changing the resistivity of the device, and leading to an increase in the current. A measure of a photoconductor's efficiency is its responsivity, usually defined as the number of amperes of current per watt of incident light or the number of carriers generated per photon.

Most photoconductors made with semiconductors have a responsivity at very low temperatures that shows a strong dependence on the lifetime of the photogenerated carriers. Germanium doped with beryllium is used to make detectors for wavelengths smaller than 50 microns ($E > 25$ meV). These devices are typically operated at temperatures between 2 and 5 Kelvin.³ At these low temperatures, though, the responsivity of most standard, shallow impurity-doped photoconductors does not exhibit a very strong temperature dependence. The sample 710-9.5 (figure 3) shows the responsivity of a typical photoconductor made from Ge:Be. Alexander, Baron, and Stafsudd⁴ have shown that the responsivity of photoconductors doped with deep impurities depends very strongly on the degree of compensation of the residual shallow levels. Near exact compensation of the shallow levels the responsivity becomes strongly temperature dependent as shown in figure 3 for Ge:Be sample 706-14.3.

The creation of such closely compensated crystals is of great interest because of the large responsivity. But, since the control of impurities to one part in ten trillion is not easy, research must be carried out that will

enable one to grow crystals within such tolerances. Here, we will investigate the hole concentration of germanium with shallow and deep levels present. We expect to find that the increase in responsivity is reflected in an increase in the free hole concentration when light is incident on a sample. We will show this is a result of an increase in the lifetime of free carriers due to a change in the number of ionized traps. The technique of photo Hall effect is ideally suited to study the lifetime changes as a function of doping and temperature.

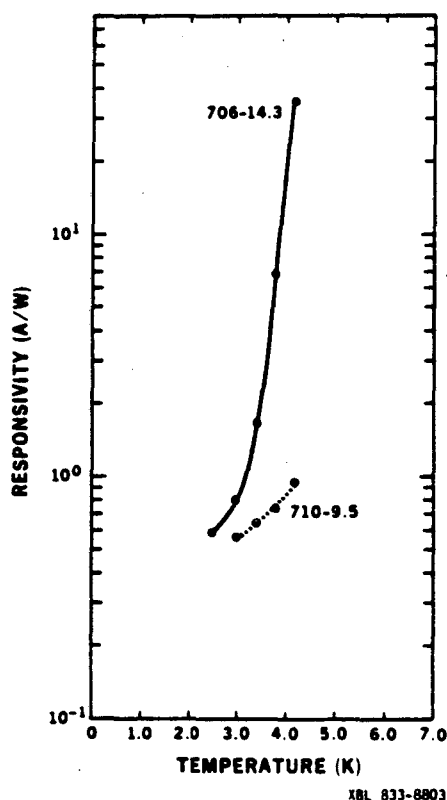


Fig. 3: The responsivity of photoconductors. The behavior of sample 710-9.5 is characteristic of most photoconductors. Notice in contrast the large increase in the responsivity for sample 706-14.3, whose shallow acceptor concentration is very close to the net donor concentration (close shallow level compensation).

2. THEORY

2.1 Carrier concentration (qualitative)

To understand what contributes to the hole concentration at different temperatures and different impurity concentrations, let us view it qualitatively so that we can see what processes are taking place. In Section 2.2, we shall derive the equations and then show that they support this basic picture. Consider a system with two acceptor levels and one compensating donor level. Let N_1 be the concentration of an intentionally added semi-deep dopant ($10^{15} - 10^{16} \text{ cm}^{-3}$) and let E_1 be its ionization energy (20-30 meV). Let there be a much smaller concentration N_2 of a residual shallow acceptor with energy E_2 (11 meV). Finally, let N_D be the net concentration of compensating donors. We will, for convenience, define K to be the compensation N_D/N_1 . Because, as we shall see, the shallow acceptor acts to compensate the donors by making the donor concentration appear to be smaller, we shall define a "shallow compensation" $K_S = N_2/N_D$. We will define over-compensation to mean $K_S > 1$ and under-compensation to mean $K_S < 1$. Thus, we have

$$\begin{aligned} N_1 &\gg N_2, \quad 0 < K < 1, \\ N_1 &> N_D, \quad 0 < K_S, \\ E_1 &> E_2. \end{aligned} \tag{4}$$

Figure 1 illustrates the energy level diagram for this system. Holes that exist in the valence band are considered to be free with an effective mass of 0.35 times the mass of an electron.⁵ Since the donor levels are all far above the Fermi level, they remain ionized at all temperatures.

Let us first consider the case where $N_2 < N_D$. At high temperatures (but not high enough to excite a significant number of electrons or holes across the bandgap) we find all the acceptors ionized, and therefore find $N_1 + N_2 - N_D$ holes in the valence band since N_D acceptors are ionized due

to compensation. At $T = 0$, we can see that the state with least energy is that in which all of the shallow acceptors are ionized and the remaining $N_D - N_2$ of the deeper acceptors are ionized. This argument simply follows from charge neutrality and the fact that all the donors remain ionized. The free hole concentration at $T = 0$ is zero.

As one raises the temperature, the remaining neutral deep acceptors begin to ionize and contribute holes to the valence band. In simple terms, this system (since the shallow acceptors remain ionized all the time) appears as though it contains only the deeper acceptors and $N_D - N_2$ compensating donors, making determination of the actual donor concentration rather difficult using the dark Hall effect which only measures the thermal generation of carriers. By means of simple rate statistics arguments,⁶ and given that there are p holes to recombine into $p + N_D - N_2$ ionized sites, the free hole concentration can be determined with

$$p (p + N_D - N_2) = C e^{-E_1/k_B T}, \quad (5)$$

where C is some constant. Consider two regimes: $p \ll N_D - N_2$ and $p \gg N_D - N_2$. In the first regime, encountered at lower temperatures, we see that p is proportional to $e^{-E_1/k_B T}$, which is commonly referred to as "full-slope freezeout." In the other regime we find that p is proportional to $e^{-E_1/2k_B T}$, which is commonly referred to as "half-slope freezeout."

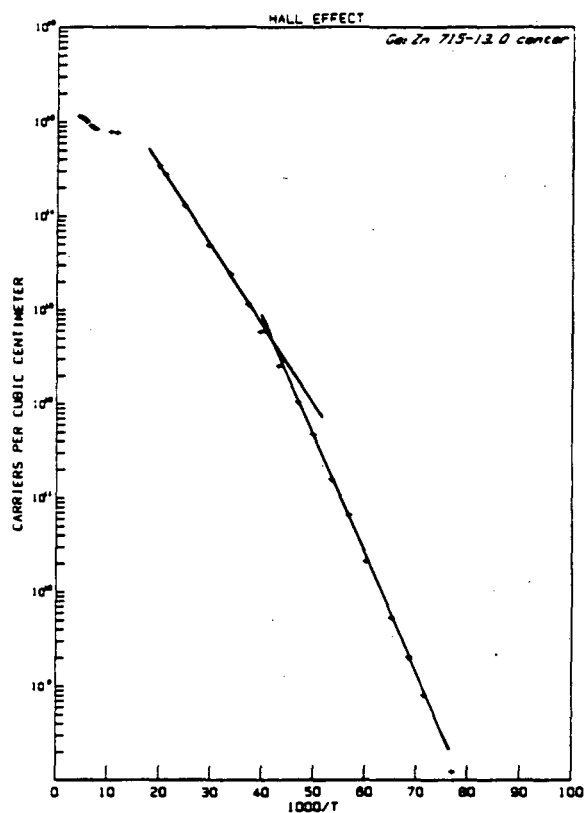
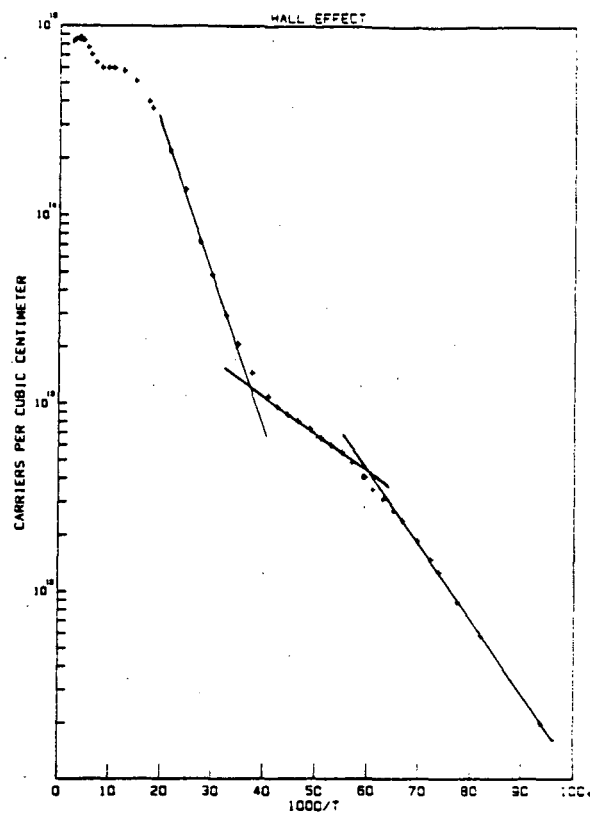
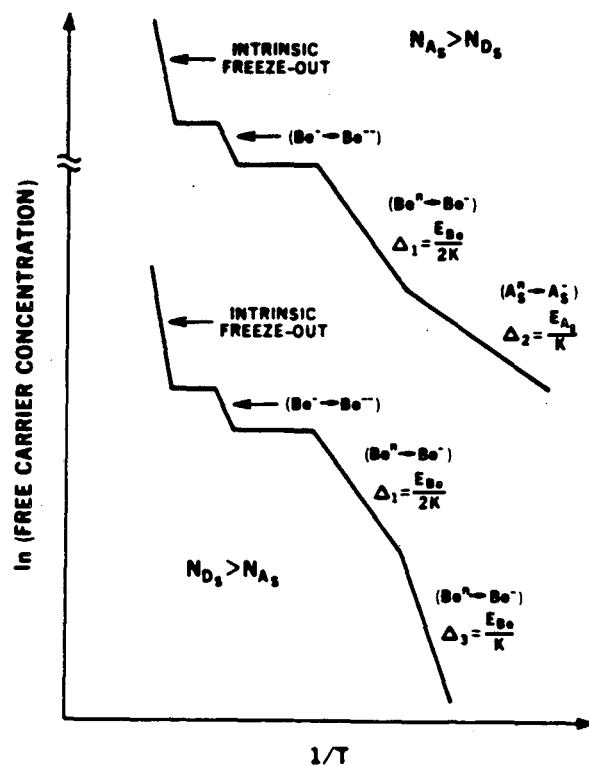
Figure 4(a) illustrates data of this type. The data are typically plotted on an Arrhenius plot ($\ln p$ vs. $1/T$) to show the two regimes, and the energy of the level can be found by finding the slopes of the two regimes.

In the case where $N_2 > N_D$, we have a rather different situation. Here, at $T = 0$, we see that if $p = 0$, then only $N_2 - N_D$ of the shallow acceptors are ionized. Also, if the temperature is low enough so that very few of the deeper acceptors are ionized, then the system would behave as if it had N_2 shallow acceptors and N_D compensating donors. We should then

observe the full and half slope freezeouts of the shallow acceptors as explained above, at least until the temperature becomes high enough to begin ionizing the deep acceptors, in which case the half-slope freezeout caused by E_1 will dominate. Figure 4(b) shows data illustrating the freezeout of such a system.

When light of frequency great enough to ionize either the shallow or deep acceptors shines on the sample, the situation changes. We consider a simplified situation where we assume the capture cross section σ_c of an ionized acceptor is essentially the same regardless of species. This assumption will later be made more general. If $N_2 < N_D$, then our situation has a number of regimes. At very low temperatures, if the number of photons is small enough, the deep acceptors tend to be ionized. As a result, most of the shallow acceptors become neutral since, at $T = 0$, there is no thermal ionization and very little photoionization of them. The ionized shallow acceptor concentration becomes negligible and so N_1^- can essentially be considered to be $N_D + p$. If we are ionizing g_{opt} centers per second per unit volume, then we can define a lifetime τ such that $p = g_{opt}\tau$. The lifetime τ can be considered to be inversely proportional to the number of ionized deep acceptors. Thus, at low temperatures τ is inversely proportional to $N_D + p$.

If the temperature is raised, then we reach a point at which the shallow acceptors become thermally ionized. In this case, free holes are created which recombine with the semi-deep ionized acceptors, lowering N_1^- . When all the shallow acceptors are ionized thermally, then N_1^- becomes $N_D + p - N_2$. Since N_1^- drops, the lifetime increases, and p decreases. (Note: g_{opt} is small enough so that p is much smaller than N_D). We would thus expect a step in the concentration proportional to $(p + N_D)/(p + N_D - N_2) = N_D/(N_D - N_2)$, caused by this lifetime change. This effect is

(a) Data showing the case $N_D > N_A$ (b) Data showing the case $N_D < N_A$ 

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(c) Schematic showing freezeout of different levels.

Fig. 4: The freezeout of carriers from dark Hall effect.

usually not visible in most semiconductors because it is very difficult to attain such similar concentrations and the precision of most Hall effect measurements is not high enough. The closer the shallow compensation is to unity, the larger the step. It must be understood that this lifetime step results only when a population inversion is created by optical pumping. This effect does not exist when there are no photons incident on the sample.

As the temperature is raised further the deeper acceptors become thermally ionized and contribute holes to the valence band. These thermally generated holes quickly obscure the effects of the photons. When it happens, we say that the hole concentration is "thermally dominated" rather than "photon dominated."

This lifetime step cannot be observed by measuring the number of free carriers with the Hall effect when $K_S > 1$. Notice that the lifetime step occurs when the shallow acceptors become ionized. But in the case, $K_S > 1$, the thermal contribution to p is dominated by these acceptors. The concentration step is consequently hidden by the thermal generation of carriers. The concentration is best expressed as $p = p_{\text{therm}} + g_{\text{opt}}t$. The photo Hall effect can only be used to measure the lifetime in the regime where p_{therm} is insignificant. The effect of the lifetime change can be observed with photoconductivity measurements which measure dp/dI instead of p .

2.2 Carrier concentration (quantitative)

All of the above can be made more quantitative. If we neglect the effects of excited states, as mentioned above, then we can write down the equilibrium rate equation for the i -th acceptor species,

$$N_i^0 \langle \sigma I \rangle_i + N_i^0 b_i N_V \exp(-E_i/k_B T) = p g_i b_i N_i^-, \quad (6)$$

which states that the number of acceptors ionized per second is equal to the number that recombine per second. The first term of equation 6 states that the number of holes that are photoionized is proportional to the product of

the number of neutral acceptors N_i^0 , the photon cross section of the neutral acceptor σ , and the flux of photons. The second term states that the number of holes that are thermally ionized is proportional to the product of the number of neutral acceptors N_i^0 , the effective number of states into which the holes will be ionized N_v , and the Boltzmann factor. The constant of proportionality is the recombination coefficient for the capture of holes by ionized acceptors B_i , as shown by Blakemore.⁷ The right-hand side of the equation states that the number of holes that recombine is equal to the product of the recombination coefficient B_i , the number of holes p , and the number of states into which those holes can recombine. The latter is given by the product of the degeneracy g_i (assumed to be 4 for acceptors in germanium) and the number of ionized acceptors N_i^- . $\langle \sigma I \rangle_i$ is given by⁸

$$\langle \sigma I \rangle_i = \int_0^\infty \sigma_i^{\text{opt}}(\lambda) I(\lambda) d\lambda = \frac{1}{d} \int_0^\infty n_i(\lambda) I(\lambda) d\lambda. \quad (7)$$

where $I(\lambda)$ is the number of photons per second per unit area of wavelength λ incident on the sample, σ_i^{opt} is the optical cross section of the impurity, n_i is the quantum efficiency, and d is the sample thickness.

Since $N_i = N_i^0 + N_i^-$, the above rate equation may be solved to obtain

$$N_i^- = \frac{N_i}{1 + \frac{g_i p}{N_v \exp(-E_i/k_B T) + \frac{\langle \sigma I \rangle_i}{B_i}}}. \quad (8)$$

By charge neutrality, the number of donors and the number of holes is equal to the number of ionized acceptors, leading to

$$p + N_D = \sum N_i^- \quad (9)$$

since the free electron concentration is negligible by the law of mass action. Equations 8 and 9 are the main equations governing the system of n acceptor levels. They are easily solved numerically and give various

different characteristic solutions depending on the relative concentrations of N_i and N_D as was demonstrated above. For this research, we are concerned primarily with systems with two acceptor levels. For high temperatures (about 300K for germanium) and no photon flux we have (see Appendix B)

$$p = N_i + N_2 - N_D \quad (10)$$

as was shown above. For the regime where $p \gg N_2 - N_D$ we have

$$p = \sqrt{\frac{N_1 N_v}{4}} e^{-E_1/2k_B T} \quad (11)$$

For lower temperatures and $N_D > N_2$, we have

$$p = \frac{N_1 N_v}{4(N_D - N_2)} e^{-E_1/k_B T} \quad (12)$$

If we solve equations 11 and 12 for T and p , we can find where the two curves intersect:

$$p_{int} = N_D - N_2 \quad (13)$$

Equation 13 allows us to easily read from a graph of data the value of $N_D - N_2$.

When we consider photoexcitation in this system, we add the photon generation term into equation 6. When the temperature is very small, the thermal term becomes negligible for both acceptors and

$$\begin{aligned} p &\approx \frac{N_1 \langle \sigma I \rangle_1}{4(p + N_D) B_1} + \frac{N_2 \langle \sigma I \rangle_2}{4(p + N_D) B_2} \\ &\approx \frac{N_1 \langle \sigma I \rangle_1}{4(p + N_D) B_1} \end{aligned} \quad (14)$$

Since it is possible to use a small enough photon flux to make $p \ll N_D$, we can use this equation to find N_D . This fact is useful since, as we found earlier, N_D or N_2 cannot be found independently from dark Hall effect measurements. If $N_2 < N_D$, we find that there is another regime where thermal generation is negligible for the deep acceptor but dominant for the shallow acceptor. In other words, the full ionization of shallow acceptors leads to

$$p = \frac{N_1 \langle \sigma I \rangle_1}{4B_1(p + N_D - N_2)}. \quad (15)$$

To calculate where the step in the hole concentration occurs, we can find where the ionized shallow acceptor concentration is equal to the neutral shallow acceptor concentration, assuming that there is no photogeneration of shallow acceptors:

$$T = \frac{E_2}{k \ln \left[\frac{N_v}{gp} \right]}. \quad (16)$$

This step in the concentration, as explained earlier, is caused by a change in the number of deep ionized acceptors. Figure 5 illustrates these regimes as generated by a computer assuming that B_1 is temperature independent and none of the shallow acceptors are photoionized. The different curves correspond to different degrees of shallow compensation. The two ionized acceptor concentrations are displayed to demonstrate where the shallow acceptors become ionized and where the concentration of the deep ionized acceptors drops. Note that the impurity concentrations are the same for figure 5(a) and (b), yet for figure 5(b) the step in concentration is partially masked by the onset of thermal carriers. The large photon generation rate forces the temperature given by equation 16 to be too high to be observed. It thus became a problem to see this step for the first experiment with sample 728-4.3 (see figure 15).

2.3 Temperature dependence of the recombination coefficient

All of the graphs in figure 5 assume that there is no temperature dependence of the recombination coefficient B_1 . We generally consider B_1 to be the product of the average thermal velocity of carriers $\langle v \rangle$, and the capture cross section σ_c , where

$$\begin{aligned} \langle v \rangle &= (3k_B T / m^*)^{1/2} \\ (m^* &= 0.35 m_e) \end{aligned} \quad (17)$$

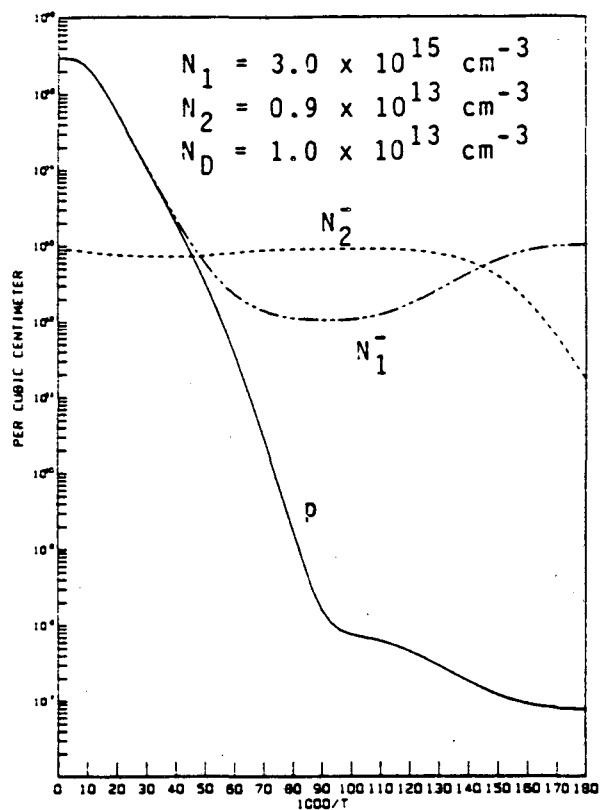
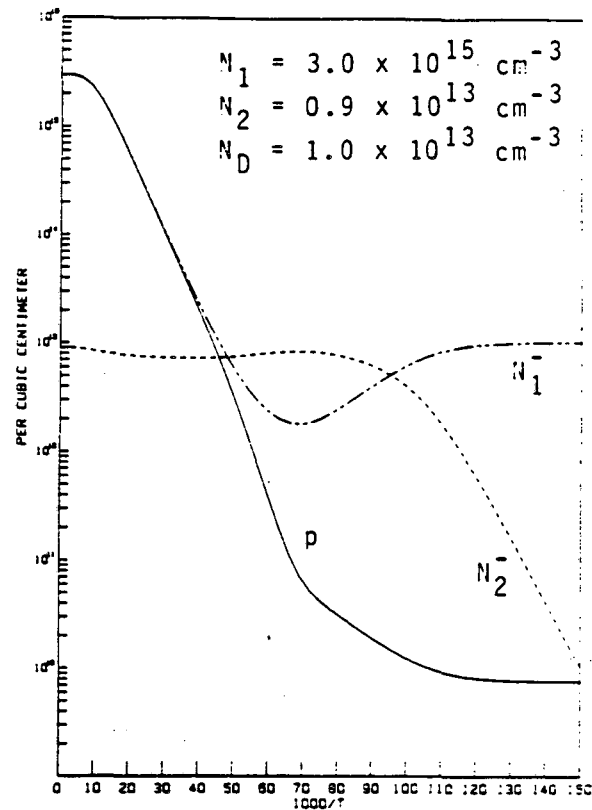
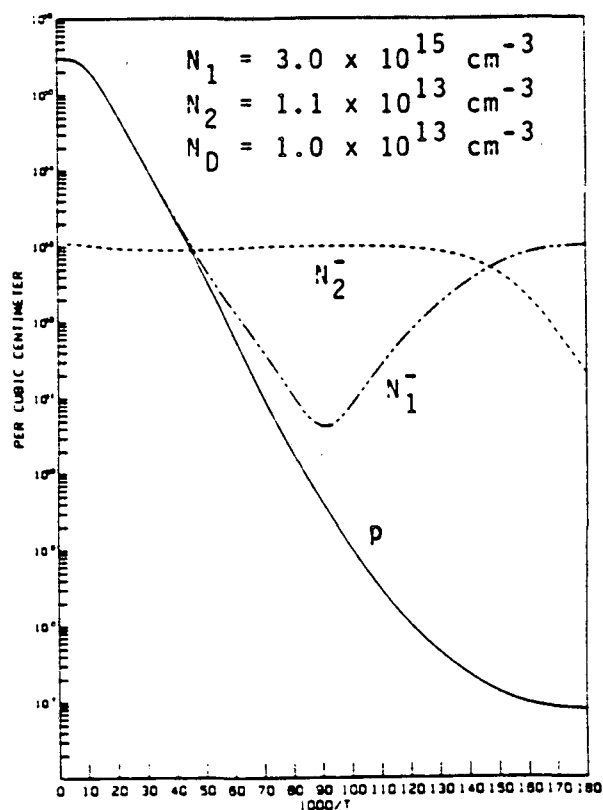
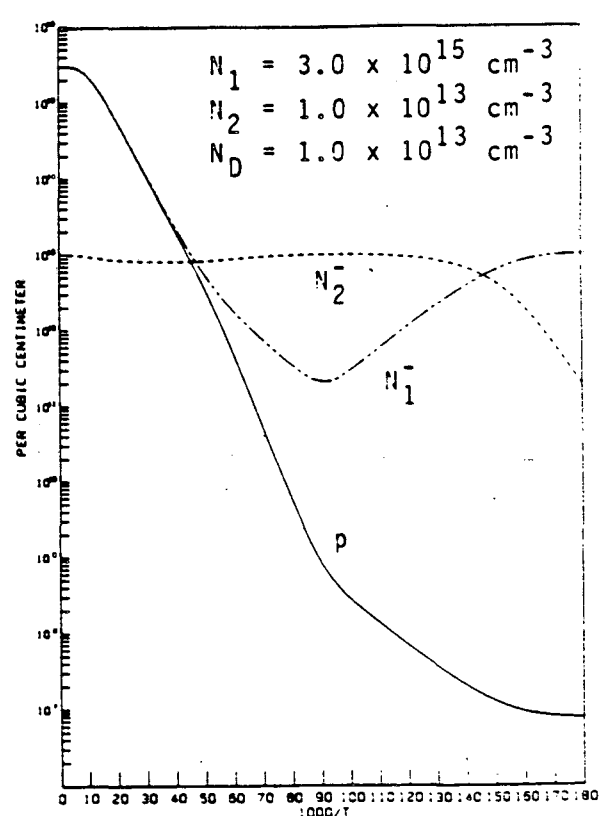
(a) $N_A < N_D$ (small flux)(b) $N_A < N_D$ (large flux)(c) $N_A > N_D$ (small flux)(d) $N_A = N_D$ (small flux)

Fig. 5: Effects of different amounts of shallow compensation on the hole concentration when samples are illuminated.

is itself temperature dependent. Similarly, one would expect the cross section to be temperature dependent since the ability for the ionized acceptors to capture a free carrier into one of its excited states increases as the thermal energy of the system decreases. Attempts have been made to derive this cross section. A theory by M. Lax⁹ explains the process by a model of cascade capture whereby a carrier is first captured by a center in its bound excited states and then, through a process of acoustic phonon collisions, relaxes into its ground state. Lax considers the probability that an electron is captured into excited states and then becomes free before the electron decays into the ground state (reemission). His theory leads to an approximate temperature dependence of about T^{-4} . Abakumov et. al.¹⁰ made modifications to Lax's theory, stating that Lax's calculation of the sticking probability was incorrect. For low temperatures ($kT < ms^2$, where s is the speed of sound in the medium), any electron that is captured into an excited state will eventually relax to the ground state. This argument leads to a T^{-1} dependence in the cross section (or a $T^{-1/2}$ dependence for the recombination coefficient). At temperatures for which $kT \gg ms^2$, the capture is dominated by long wavelength acoustic phonons leading to a temperature dependence of T^{-3} (or a $T^{-2.5}$ dependence for the recombination coefficient). Abakumov gave a single interpolating formula for the capture cross section:

$$\sigma_c = \frac{4\pi}{3I_0} \frac{e^2 Z}{\pi k T} \left[\frac{e^2 Z}{\chi(kT + 2.74ms^2)} \right]^2 \quad (18)$$

We have shown that the photo Hall effect, in conjunction with the dark Hall effect, can be useful in determining three different parameters. First, if one knows the absolute flux and the optical cross section, the cross section for the capture of holes by ionized impurities can be found, along with its temperature dependence. The values obtained can be used to test the

validity of the theories of Lax and Abakumov et. al. Secondly, the technique should be able to explain the large increase in photoresponsivity of photoconductors that are made with materials that are very closely shallow compensated. Finally, by viewing the concentration step in conjunction with dark Hall data, one can find the absolute concentrations N_2 and N_D that are not uniquely determined by the dark Hall effect alone. It may be noted here that two different approaches can be used in this last application. The first requires that a known flux is incident on the sample. Using equation 14, N_D can be found. The other approach does not require a knowledge of the flux, but is only useful when the sample is closely shallow compensated with N_D slightly greater than N_2 . From the size of the step, knowing $N_D - N_2$ from dark Hall measurements, and using equations 14 and 15, the values of N_D and N_2 can be found independently.

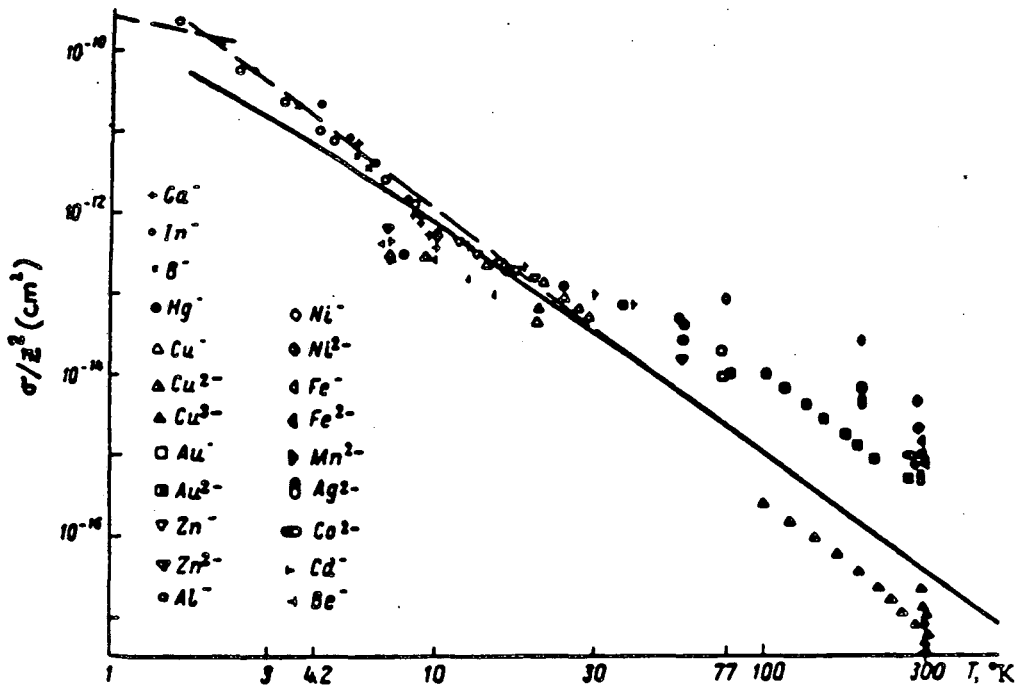


Fig. 6: The cross section for the capture of holes by different ionized acceptors in germanium (from Abakumov et. al.)

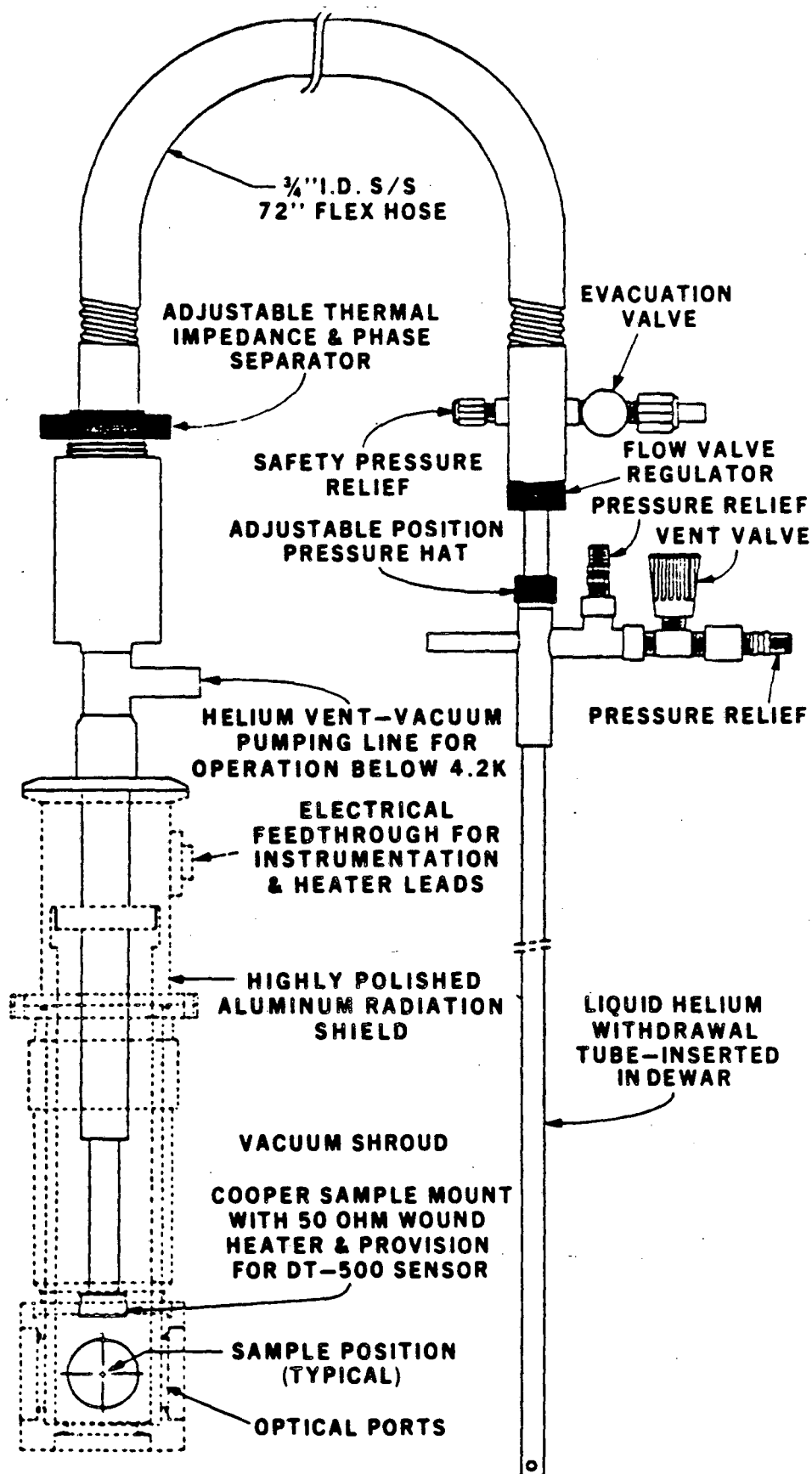
3. EXPERIMENTAL APPARATUS

The experimental apparatus used to obtain the dark Hall effect and photo Hall effect data was basically the same. It consisted of a cryogenic system that held two samples between the poles of a magnet. An automated electronics and data collection system was controlled by an HP-85 computer.

The cryogenic system (Lakeshore CT-310) is illustrated in figures 7 and 8. At one end there is an insert which fits into a liquid helium dewar, pressurized to about $3\frac{1}{2}$ psi above atmospheric pressure. The helium flows through a transfer line and into a space near the sample chamber. The helium then evaporates, exits the apparatus at the side, and flows through a flow meter. A valve at the dewar insert is used to control the amount of flow needed for cooling the samples.

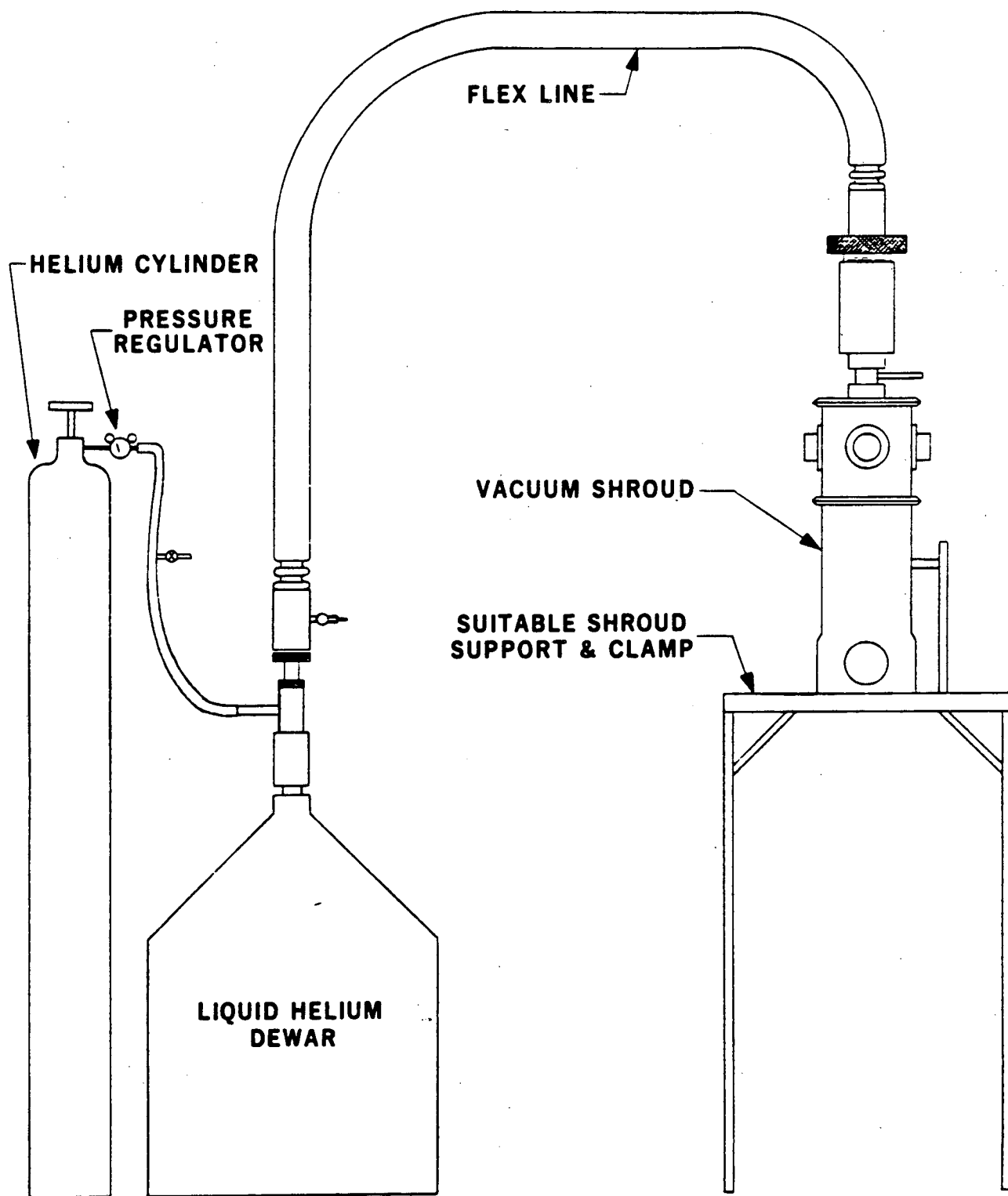
The samples themselves are attached to a copper block below the area where the helium enters. Cigarette paper and vacuum grease are used to insulate the samples electrically from the copper and to give good thermal contact. The samples are held onto the copper block with dental floss. This area, which is under vacuum to prevent heat transfer from the outside, is shielded with two radiation shields and an outer vacuum shroud. The entire system is placed so that the samples lie directly between the poles of an electromagnet. The field used for all the experiments was 1 kilogauss.

Temperature control was maintained by adjusting the flow of helium and using a temperature controller, which uses a heater in conjunction with a feedback temperature sensing diode. Temperatures were found either by measuring the voltage across a calibrated temperature diode when $10\mu\text{A}$ passes through it, or by measuring the resistance of an Allen-Bradley resistor. Three temperatures (4.2, 77, and 295K) were used to calibrate the resistor, and a fitting formula¹¹ was used to interpolate for other temperatures.



XBL 828-11242

Fig. 7: The cryogenic system showing the inside of the cryostat.



XBL 828-11237

Fig. 8: The cryogenic system showing the liquid helium dewar.

The entire system, designed by the author, is controlled by a Hewlett-Packard HP-85 microcomputer in conjunction with an IEEE-488 interface for communication with instrumentation. The system block diagram is shown in figure 9. The system handles all data collection, switch controlling, magnet controlling, data analysis and storage. The concentration values are plotted and data are stored on microdiskettes for future reference. Each measurement is taken ten times within about a half second to give an estimate of the random errors. The computer program also has provisions for adjusting the current sent through the sample so that sample heating does not occur. Generally, resistivity values were frequently checked at the next lower current setting (1/10) and adjustments were made if the results changed by more than about 5 percent. Another rule of thumb that was used was to not let the highest voltage reading go much higher than about 20mV.

Each datum point requires twelve measurements. The first four measure only resistivity with zero magnetic field. If $R_{AB,CD}^0$ is the resistance obtained by measuring the voltage V across sample corners A and B with a current I passing from corner C to D (see figure 10), $R = V/I$, then the resistivity for the van der Pauw geometry¹² is given by

$$\rho = (R_{CD,BA}^0 - R_{CD,AB}^0 + R_{CB,DA}^0 - R_{CB,AD}^0) \frac{\pi d}{4 \ln 2} \quad (19)$$

The next four measurements are Hall field measurements with the B-field in one direction, and the last four (for averaging purposes) are the same but with the field in the opposite direction. The concentration is given by

$$\rho = \frac{8B / de}{(R_{BD,AC}^+ - R_{BD,CA}^+ + R_{CA,BD}^+ - R_{CA,DB}^+ + R_{BD,CA}^- - R_{BD,AC}^- + R_{CA,DB}^- - R_{CA,BD}^-)} \quad (20)$$

Equation 20 assumes that the Hall coefficient is given by $R_H = Vd/BI = r/ne$ (in SI units), where r is the Hall factor and is generally taken to be unity for the high field limit. It is a good approximation at low temperatures. Its effects, though, can be seen in the data, especially at high temperatures,

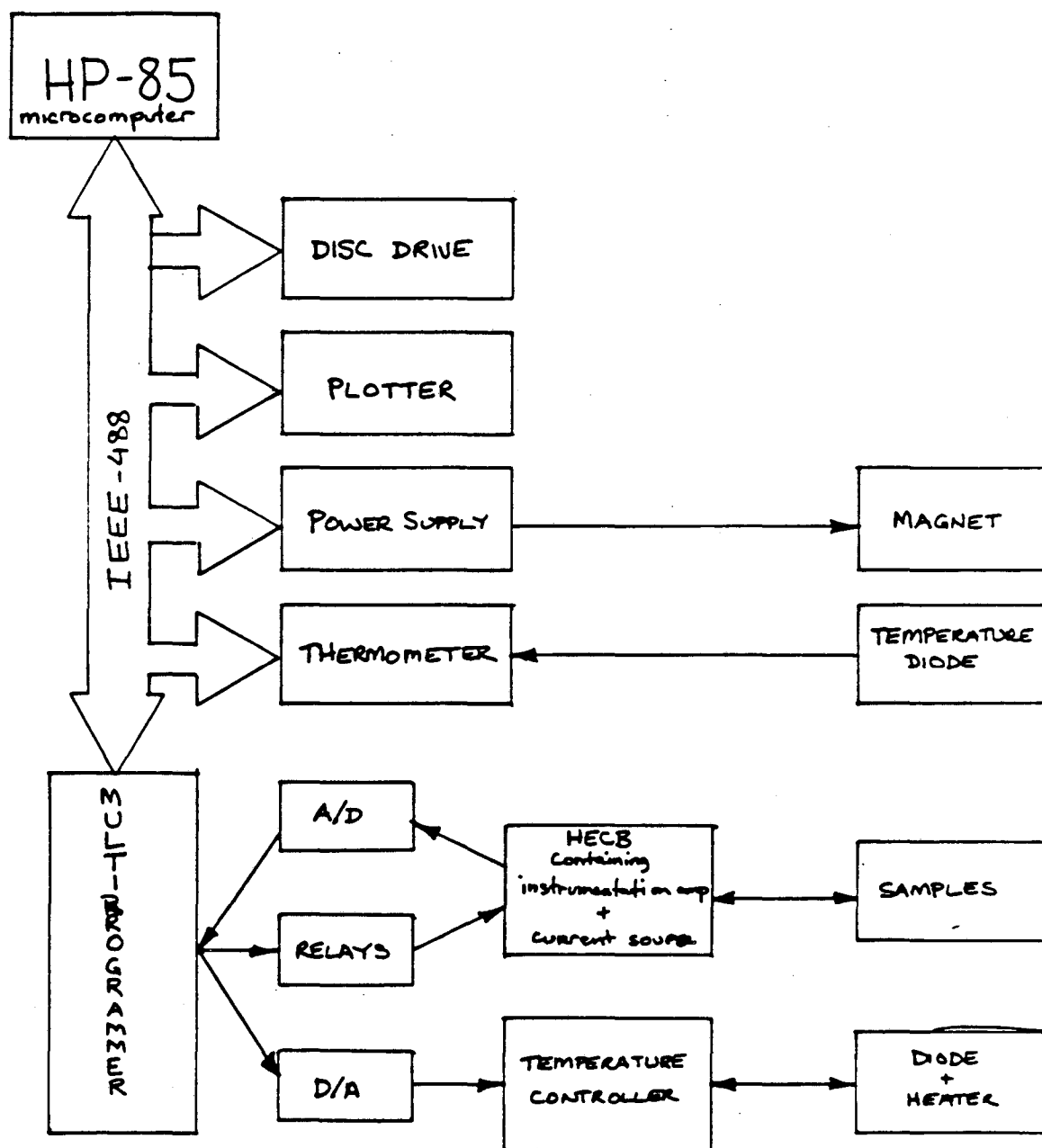


Fig. 9: The block diagram of the data collection system.

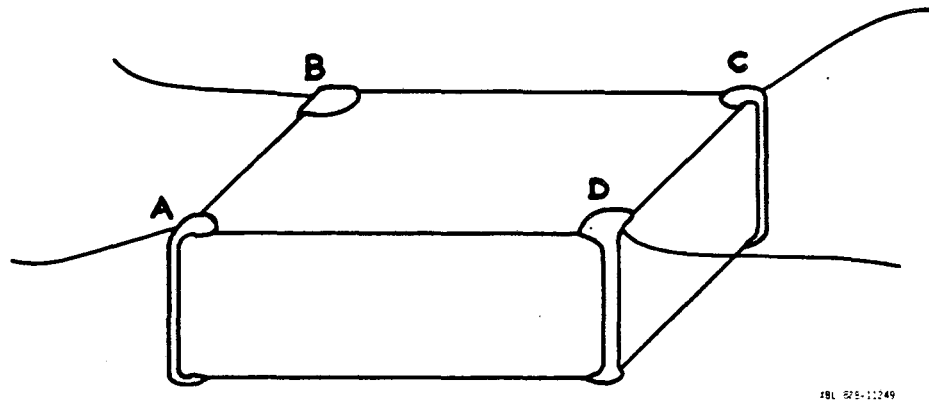


Fig. 10: Sample geometry

where it tends to cause a rounding of the calculated concentration at temperatures where the concentration should be constant. (See, for example, figures 4, 12, and 14.) This effect is partially enhanced by the fact that a discontinuity in the Hall factor, R_H , occurs when there are two different types of carriers with different Hall coefficients. At high temperatures, above 150K, the number of electrons in the conduction band becomes significant compared to the number of holes in the valence band.

The reason for taking twelve measurements is to cancel any errors that are caused by asymmetries in the sample geometry. Van der Pauw showed that errors caused by imperfect sample geometry enter only in second order with this method.

The Hall Effect Control Box (HECB) contains all the electronics that interfaces with the samples: a current source providing currents in powers of ten (10^{-2} A to 10^{-10} A), a variable gain ($\times 10, 100, 1000$) instrumentation amplifier and all the relays that control the current, gain and the current flow to the samples. The HECB is controlled by twelve relays contained in a multiprogrammer. The HECB also has an output voltage that connects to an analog-to-digital converter in the multiprogrammer for reading by the HP-85.

The magnetic field is varied with a programmable four quadrant (I-V) power supply. The computer controls the current that passes through the coils and

thus defines the field. The field is calibrated with a gauss meter. The four quadrant feature allows the field to be changed most efficiently since, to change the current, the voltage and current will have opposite polarities for a short period of time when driving the large inductance of the magnet. When the field is returned to zero, the program automatically demagnetizes the apparatus with a slowly decreasing oscillating field to eliminate any hysteresis.

The system is calibrated by measuring the true values of each of the currents and gains and finding the codes for the power supply that give the required magnetic fields. These values are entered into a file which the program reads and uses for all calculations. The advantage of this method is that it is easier to adjust the values on the computer file than it is to adjust the current values and amplifier gains so that they have exactly the ideal values.

For the photo Hall effect, there must be some way to get photons to the samples. Because of its simplicity, the light from 300K black body was chosen as the source, since the peak of its spectrum lies near the energies needed to ionize Be and Zn. The warm vacuum shroud wall was used as the 300K black body source. The question of how many photons are passed to the sample for different geometries is an important one. The decision had to be made between using an integrating cavity in which a certain number of photons pass through a hole, all of which are assumed to be absorbed eventually by centers after being reflected enough times by the walls of the cavity, or using a configuration in which the number of photons absorbed are only those that are absorbed when they pass through the crystal and are reflected out. The first is simplest to calculate; the latter requires calculating a quantum efficiency.

For these experiments, both methods were tried. The integrating cavity configuration is illustrated in figure 11(a). An aperture of diameter 0.15 cm

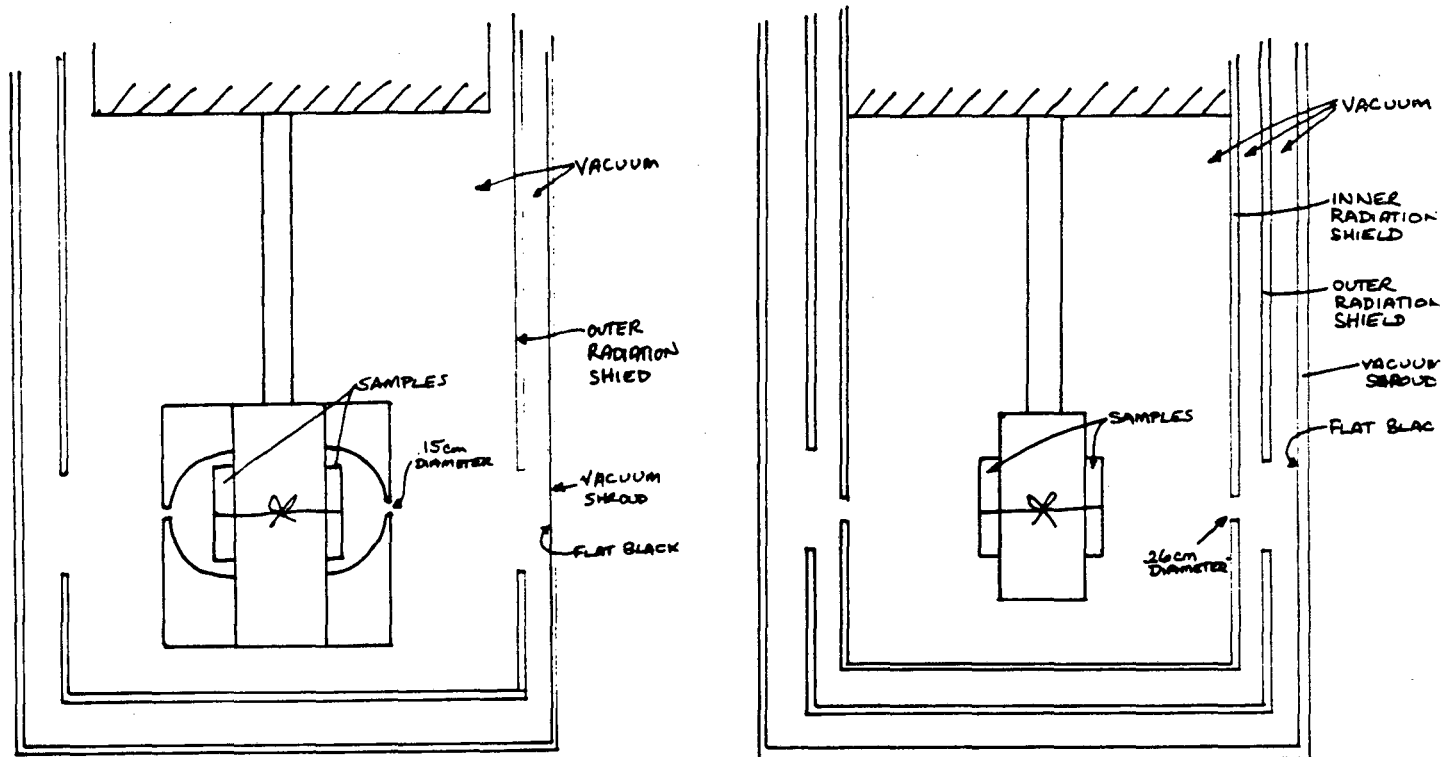
looks out at the inside of the outer vacuum shield which has been painted with "flat black." We assume that the emissivity of the wall is unity. The cavity consists of a hemispherical dome made of polished brass. The idea is that any light that is reflected by the front surface of the sample is reflected back towards the sample again. This assumption turned out to not be very good. If we evaluate the recombination coefficient assuming this configuration, we obtain a value at least an order of magnitude from that published by Abakumov.¹⁰

The other method tested (and used for subsequent measurements) is illustrated in figure 11(b). Here, we assume that the light passes through the front surface (where some light is reflected), gets reflected from the back surface, and then passes out the front (at which point some gets reflected back again). During this process, there is an absorption coefficient $\lambda = N_A^0 \sigma$ where σ is the optical cross section of the impurity at its ionization energy given approximately by $\sigma = 2.5 \times 10^{-18} / E_A^2$ (Volt²).²¹ Any light that is reflected from the crystal is absorbed elsewhere. The amount of absorption by the crystal is given by the quantum efficiency

$$\eta = \frac{(1-r) [1 - \exp(-\lambda d)]}{1 - r \exp(-\lambda d)}, \quad (21)$$

where r is the reflectivity of the material (0.60 for germanium) and d is the sample thickness. This analysis gave better results for the recombination coefficient, though still almost an order of magnitude different than Abakumov's published values.

One reason for the integrating cavity's poor performance is the electrically insulating cigarette paper and vacuum grease at the back of the crystal which probably absorbs a large amount of the light. The contacts also provide a strong absorbing medium. Furthermore, much of the light may



(a) Integrating Cavity

(b) Open sample chamber

Fig. 11: Illumination techniques

have been reflected straight out the aperture through which it entered. Our assumption that all the photons are absorbed by neutral acceptor impurities is clearly inadequate. The open sample chamber method, however is not without fault. Early experiments indicate that only a small amount of dirt (usually stray vacuum grease) would significantly alter the results, both by absorbing light as well as changing the reflectivity. Therefore, the cleanliness of the front surface is important. It is also important that the total quantum efficiency be integrated, taking into account the black body spectrum and the energy dependence of the photon capture cross section as in equation 7. For the experiments that were carried out here, the value for σ given above was used as the cross section, since its energy dependence was not known.

3.2 Sample preparation

Samples were cut from the crystal into $6 \times 6 \times 1 \text{ mm}^3$ square plates. The orientation of the $6 \times 6 \text{ mm}^2$ surface of the samples is $\langle 113 \rangle$, the same as the growth direction of the crystal. The samples were lapped with 600 grit until all of the saw marks are gone on all sides and edges. The corners were lapped flat, creating four extra faces of about 1 mm^2 each. After this, the samples were cleaned in deionized water to get rid of any excess grit. The water was removed with methanol. Samples were then etched in a solution containing 7 parts nitric acid, 2 parts hydrofluoric acid, and 1 part fuming nitric acid for about 30 seconds. At the end of etching, the samples were quenched with deionized water, and finally rinsed in methanol.

Indium alloy contacts were applied to the four corners. This creates a heavily doped p-type region allowing injection of carriers. If this process is done poorly (too low temperature, oxides, etc.), it results generally in poor signal to noise behavior since, if the region is not heavily doped, there will not be a good ohmic contact at low temperatures. The region must be heavily enough doped so that holes can tunnel through the barrier to allow for conduction even at low temperatures. The process consists of applying a small amount of indium to the contact area with a large soldering iron, making sure that both the indium is melted and the sample gets hot enough for wetting to occur. The soldering iron is generally moved back and forth a small amount so as to assure that the entire contact is wetted. This process is done for about 30 seconds for each corner. After all the corners are wetted with indium, wires are then attached. During this entire process, it is important that the sample be kept clean; holding the sample in a small vise with clean filter paper usually suffices.

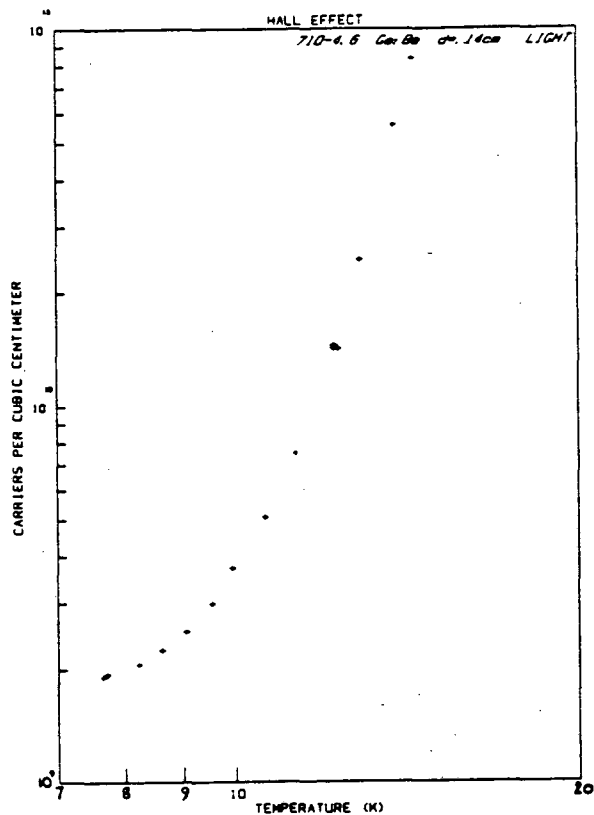
4. EXPERIMENTS AND INTERPRETATION OF DATA

4.1 Obtaining the capture cross section of ionized beryllium sites

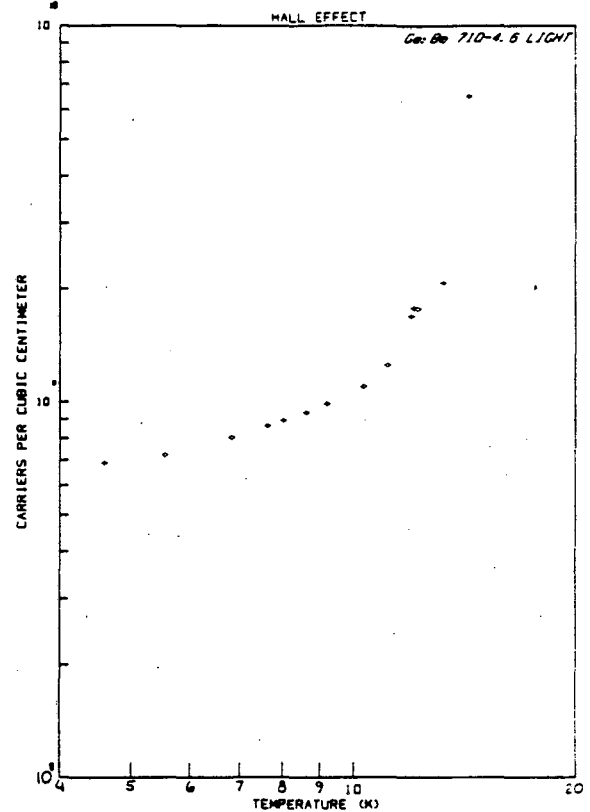
The goal of the early experiments was to determine the capture cross section of ionized beryllium sites. The importance of doing this was twofold. First, the assumptions made about the number of photons absorbed by the neutral beryllium sites had to be tested. Second, the value of the capture cross section should be found by a different method than had been found previously. Early experiments in the 1960's were carried out using recombination noise spectra to find the lifetime of free carriers.^{13,14} Since this requires measuring the noise levels in the 100 MHz range, it would be a good test to measure the same quantities independently by a very different method. It would also be useful to find the temperature dependence of the cross section and compare the value obtained with Lax's and Abakumov's theories.

To find the capture cross section, crystal 710-4.6 was used since, from dark Hall measurements, it was shown to have a rather high donor concentration of about $5 \times 10^{12} \text{ cm}^{-3}$. Since the shallow acceptor concentration ($N_S = 10^{11} \text{ cm}^{-3}$) is usually not high in high purity crystals, we can assume that it is much below N_D . With the integrating cavity, there were 2.5×10^{17} photons per second incident on the sample which measured $0.58 \times 0.58 \times 0.14 \text{ cm}^3$. The data for the photo Hall effect are given in figure 12(a). At 8K, (assuming complete absorption by neutral acceptors) the recombination coefficient was found to be $2.4 \times 10^{-5} \text{ cm}^3/\text{sec}$ ($B_{Be} = 8 \times 10^{-12} \text{ cm}^2$).

When using the open sample chamber method for determining the photon flux, a total flux of 3×10^{16} photons was incident on the sample, giving a generation rate of $5.8 \times 10^{16} \text{ cm}^{-3}/\text{sec}$. The data for the photo Hall measurements are given in figure 12(b). At 8K, the recombination coefficient was found to be $1.3 \times 10^{-5} \text{ cm}^3/\text{sec}$ ($B_{Be} = 4.2 \times 10^{-12} \text{ cm}^2$). This



(a) With integrating cavity



(b) With open sample chamber

Fig. 12: Photo Hall effect data used for calculating cross section

value is much closer to the $\sim 3 \times 10^{-13} \text{ cm}^2$ given in the paper by Abakumov.

The temperature dependence of the recombination coefficient is given by the slopes of the photon dominated regions when the data are plotted in a $\log p$ vs. $\log T$ graph. The value obtained for the integrating cavity method was $T^{-2.6}$ and the value obtained for the "single pass" method was $T^{-0.7}$. The errors on these are fairly high since there is not a single line that passes through the data as plotted. Two reasons may account for this. First, according to Abakumov, there should be a transition from the T^{-3} region to the T^{-1} region for the cross section, and (see figure 6) it can be seen that the values found earlier for beryllium indicate that the transition is in this temperature range. Second, carriers may be excited to a point far above the valence band edge by photons of energy $E > E_{be}$ since no filters were used to

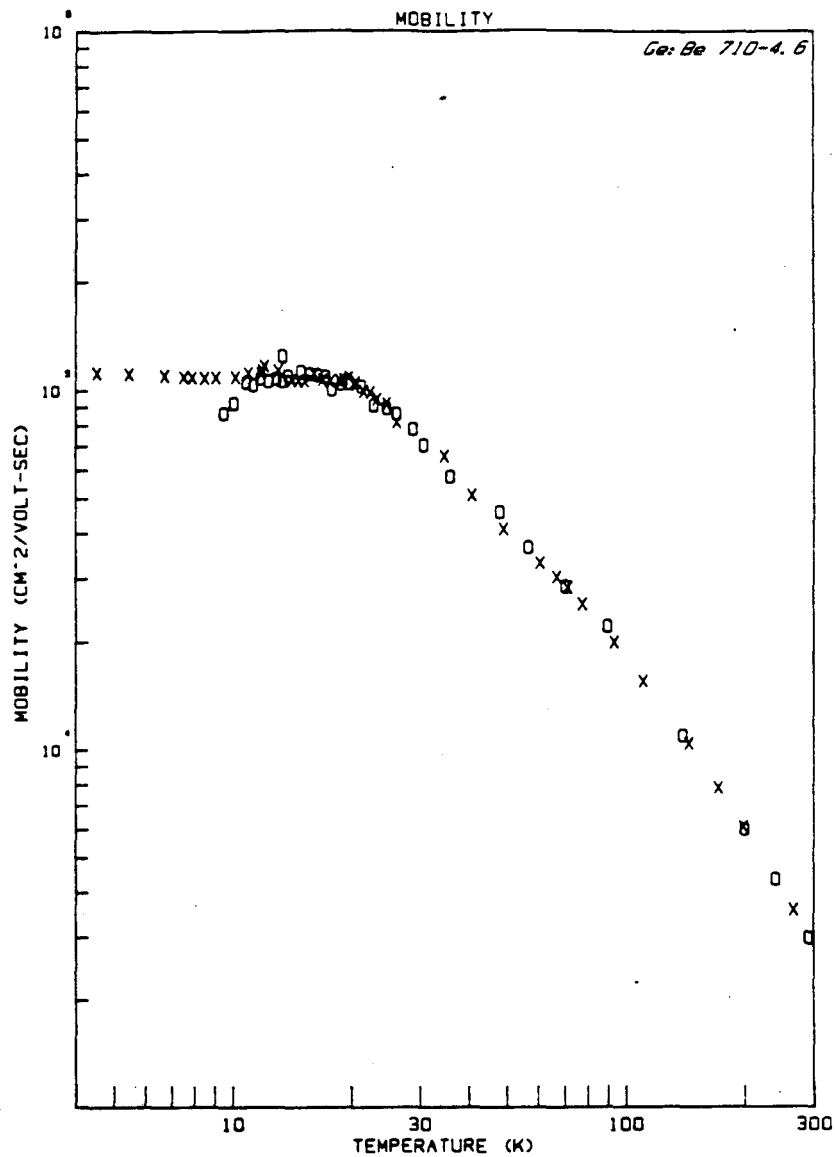


Fig. 13: Mobility of carriers in photoillumination (crosses) and in the dark (circles).

exclude higher energy photons. The effects of this can be seen by considering the mobility of carriers at low temperatures. Ideally, there should be no difference between the mobility measured with the dark Hall effect than with the photo Hall effect. But as figure 13 shows, the mobility of carriers is quite a bit higher when measured with the photo Hall effect than with the dark Hall effect at low temperatures, indicating that high mobility carriers are being generated.

4.2 Crystals with closely compensated shallow levels

Since no beryllium doped germanium crystal existed at the beginning of these studies with the characteristics needed to see a lifetime shift in the photo Hall effect, a special crystal had to be grown. To grow the appropriately doped crystal is not trivial, though, as one must in some way add a small amount of shallow acceptors or donors in anticipation of the amount of trace impurities that are not intentionally added. The problem is that of exactly doping a crystal with about $5 \times 10^{15} \text{ cm}^{-3}$ beryllium atoms, and also adding enough other impurities so that $N_D = N_{Sh} = 10^{12} \text{ cm}^{-3}$, i.e. one part in 10^{11} . Generally, the crystal is doped by adding a measured amount of a heavily doped master alloy ($[\text{Be}] = 5 \times 10^{18} \text{ cm}^{-3}$) to a bulk of high purity material. For the crystal we wished to grow, a small portion of a master alloy of some donor had to be added to compensate the shallow acceptors such as boron and aluminum that are generally present in trace amounts.

The first attempt was to grow crystal 727. Added to 650 grams of high purity germanium was 0.47 grams of beryllium master alloy having a beryllium concentration of $2.8 \times 10^{18} \text{ cm}^{-3}$ and 2.06 grams of antimony master alloy having an antimony concentration of $4 \times 10^{18} \text{ cm}^{-3}$. The crystal, however, did not turn out as desired. From dark Hall measurements, the net acceptor concentration was clearly more than intended. One reason for this may have been that the antimony master alloy had a large concentration of other impurities.

In the second attempt, crystal 728 was grown. This time, the crystal was grown using a small amount of Ge:P master alloy, in the hope that the master alloy was better characterized. Furthermore, a new acceptor complex,¹⁵ Be-H, which acts as a shallow acceptor, would be added by growing the crystal in a hydrogen atmosphere. The beryllium hydrogen complex has the advantage of being sensitive to thermal annealing, making it possible to change the net

shallow acceptor concentration after the crystal is grown. This property allows the possibility of generating a family of curves, each corresponding to a different shallow acceptor concentration. By adding 1.16 grams of beryllium master alloy, and 9 mg of phosphorus master alloy having $2 \times 10^{18} \text{ cm}^{-3}$ phosphorus to 800 grams of high purity germanium, a crystal with the desired properties was grown. The head of the crystal has $N_D < N_{Sh}$ without annealing and $N_D > N_{Sh}$ after annealing for two hours at 600°C (see figure 14). Thus, in principle, a sample with very close shallow compensation could be made with the proper choice of annealing time and temperature.

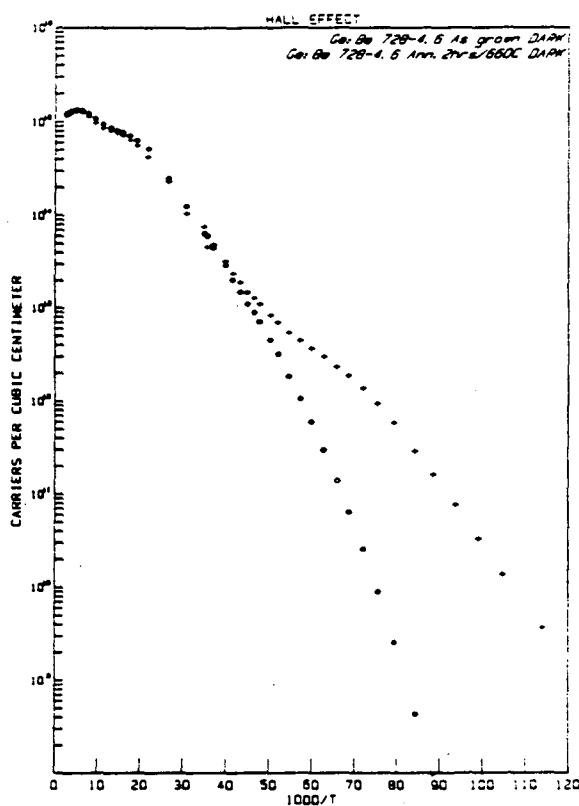


Fig. 14: Dark Hall measurements showing crystal 728 at the head as grown and after annealing at 600°C for two hours. ("+" represents "as grown" and "*" represents annealed.)

4.3 Experiments with closely compensated samples

Samples were cut from crystal 728 close to the seed end, where we knew from dark Hall measurements (see figure 14) that $K_S > 1$ in the unannealed crystal material, and $K_S < 1$ when the crystal was annealed at 660°C for two hours. Hall measurements showed $N_D - N_2 \approx 10^{12} \text{ cm}^{-3}$, which indicates that this sample may have been very closely shallow compensated, if we assume $N_D \sim 10^{12} \text{ cm}^{-3}$.

Measurements were made using the photo Hall effect on this sample with a photon generation rate of $1.4 \times 10^{17} \text{ cm}^{-3} \text{ sec}^{-1}$. Figure 16 shows the carrier concentration as a function of inverse temperature. Since the resulting carrier concentration was on the order of or greater than N_D or $N_D - N_2$, any sign of a lifetime step was hidden. From equations 14 and 15, we can see that the lifetime step becomes small if p is on the order of N_D or $N_D - N_2$. Also, as illustrated in figure 5, a large photon flux makes the step occur at a higher temperature. The conclusion was that, in order to see this lifetime step, we needed a much smaller flux of photons. There are three ways to reduce the flux. First, a filter could be used to eliminate all the photons with energies much above the ionization energy of beryllium. Second, a colder black body could be used. Third, a smaller aperture could be used. Because of time considerations and practicality, the last method was used. Here, we had to abandon the hope of having a consistent flux, but since the step in the concentration is only proportional to $N_D/(N_D - N_2)$, this consistency is not very important. Knowing this quantity, with $N_D - N_2$ obtained from dark Hall measurements, both N_D and N_2 can be found.

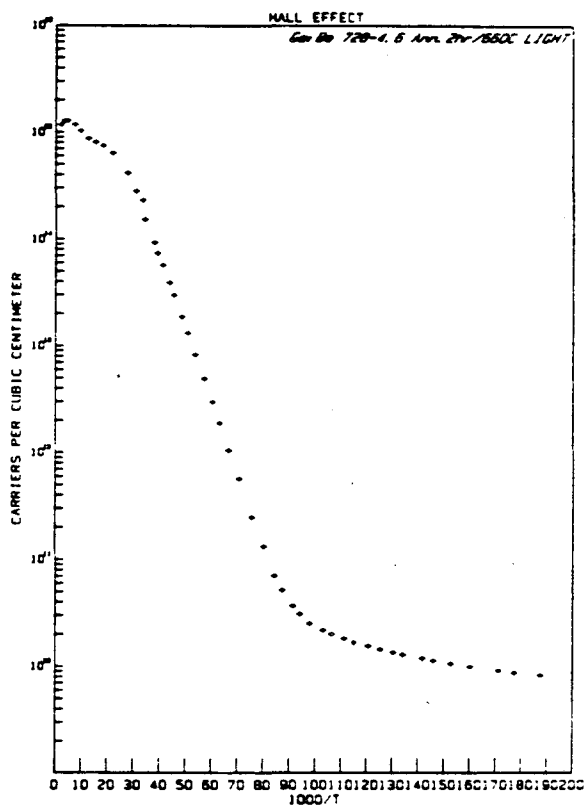
To reduce the flux, metallized tape was used to cover the holes made previously in the inner shield. A needle was then used to make a small hole with a diameter of about 0.2 mm.

The results of a number of different experiments with different annealing times are shown in figures 15, 16, and 17, and a summary of the results is given in Table 1. Since the two samples 728-4.3(1) and 728-4.3(2) were such as to give $N_D - N_2$ about 10^{12} and 10^{11} cm^{-3} respectively, the plateau of the step again cannot be seen since the step is very large. As one can see from figure 16, the carrier concentration indicates that the step begins to appear for sample 728-4.3(1). Samples 728-4.3(1) and 728-4.3(2) do illustrate, though, the strong increase in the photogenerated lifetime as the shallow acceptors become ionized. The characteristics of the data are much different than shown in sample 728-4.8(2), where the compensation is much smaller. In sample 728-4.8(2), a small increase in the concentration above the general character of the slope can be seen which is caused by the shallow acceptors becoming ionized. The step indicates that $N_D/(N_D - N_A)$ is about 1.2 - 2.

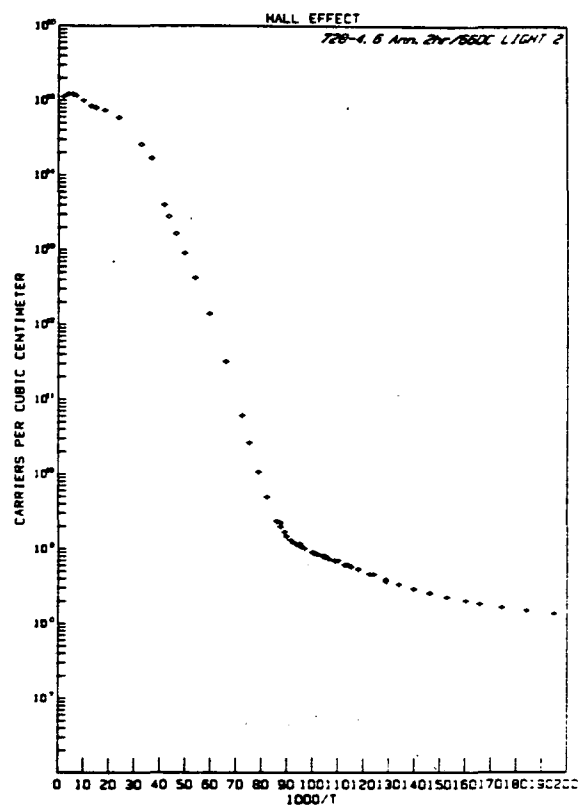
4.4 Curve fitting

The concentration of the various impurities are usually obtained by reading off the graph of the dark-Hall measurements. The various concentrations where the half-slope and full-slope regimes intersect are generally good approximations of these concentrations or differences in concentrations. Curve fitting was used by Geim, Pensl, and Schulz¹⁶ to analyze their data on Si:In and Si:Ga for both dark Hall effect as well as photo Hall effect measurements with good results. Schaub, Pensl, and Schulz¹⁷ were also able to use curve fitting to demonstrate that Si:Te is a double donor by showing that their data could not be fitted by a curve assuming only a single ionization stage.

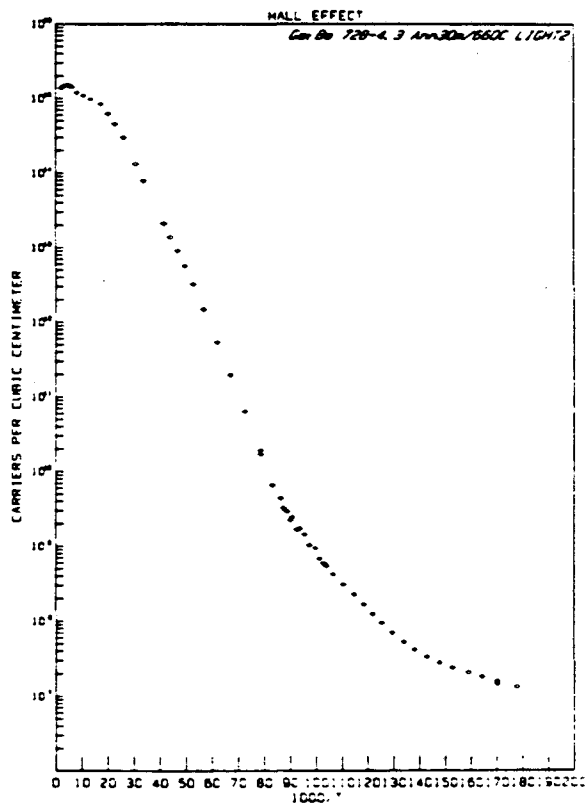
It can be seen from equations 8 and 9 that the relationship between p and T is highly nonlinear. Thus, iterative approximation techniques must be made to fit these equations to the data. Generally, the goal was to be able to fit



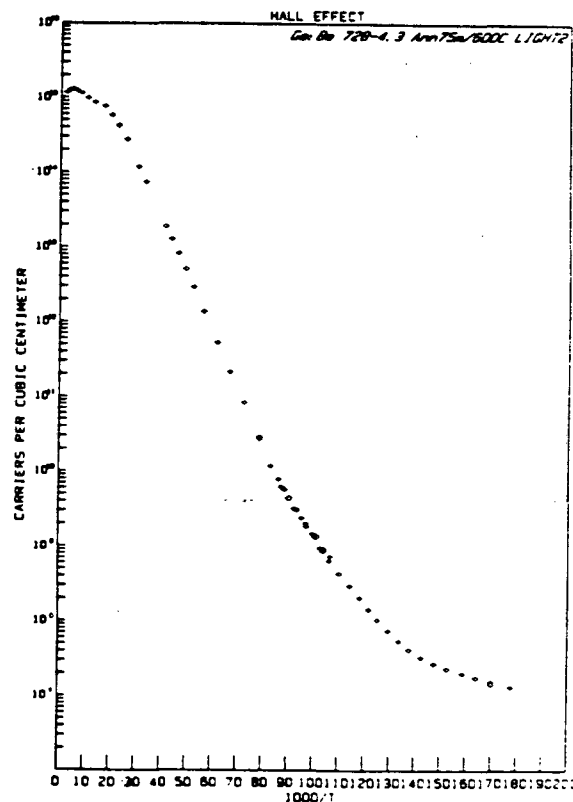
(a) Sample 728-4.8(2) with a large flux



(b) Sample 728-4.8(2) with small flux



(c) Sample 728-4.3(1)



(d) Sample 728-4.3(2)

Fig. 15: Data showing the effects of ionization of shallow acceptors on the concentration of free holes in crystal 728.

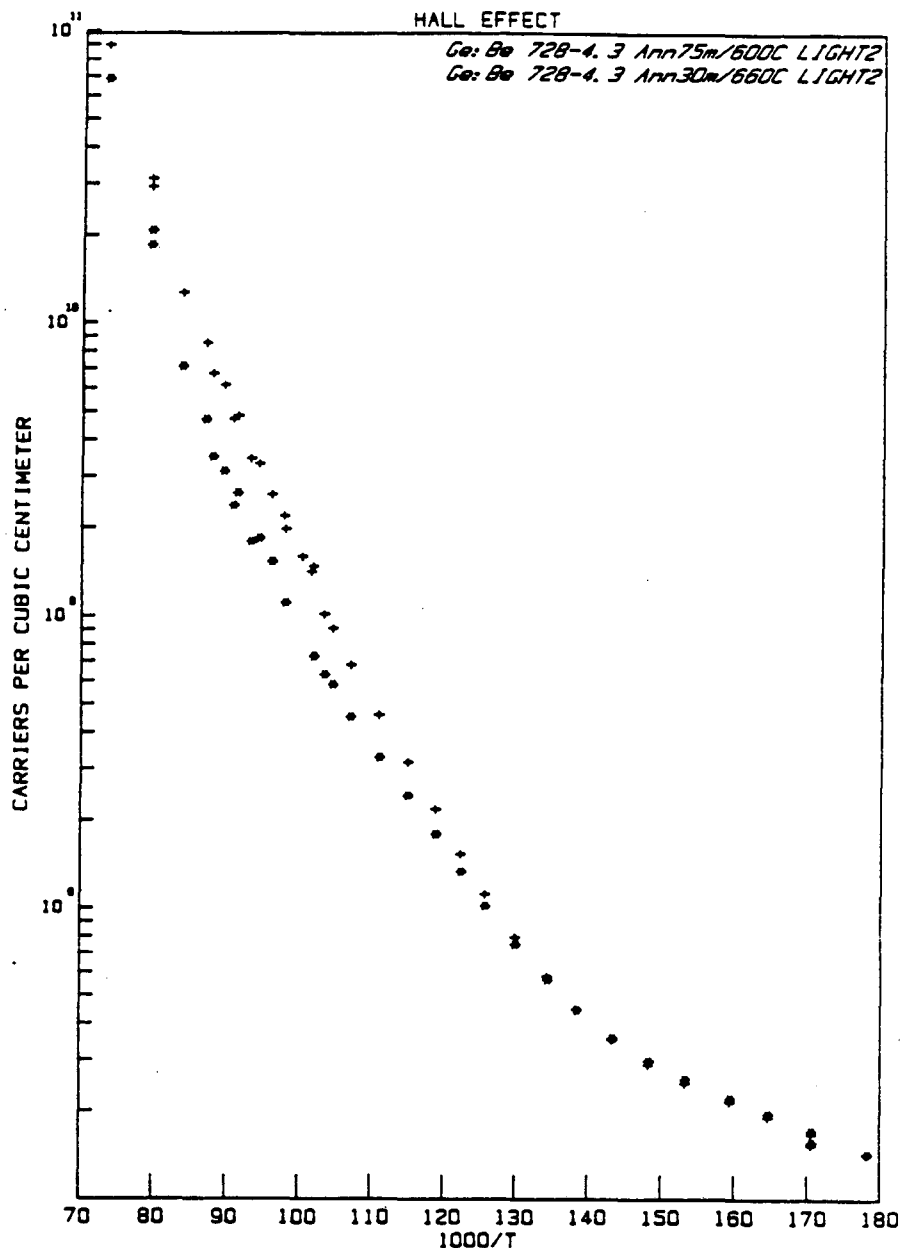


Fig. 16: The free hole concentration of illuminated samples 728-4.3(1) and 728-4.3(2), showing the region of photon dominance. Both samples are very closely compensated with $N_D - N_A$ about 10^{11} and 10^{10} cm^{-3} respectively. The sample with the lesser compensation is just beginning to show the effects of the plateau, shown by the smaller free hole concentration at the higher temperatures.

SAMPLE	ANNEALING time	temp	$N_D - N_2$	N_D	N_2	$N_D/(N_D - N_2)$
728-4.6(1)	---	---	$>10^{13}$ *	10^{12} *	$>10^{13}$	---
728-4.6(2)	120 min.	660°C	$2-6 \times 10^{11}$ *	10^{12}	$4-8 \times 10^{11}$	$1.2 - 2$ *
728-4.3(1)	30 min.	660°C	10^{11} *	10^{12}	10^{12}	>30 *
728-4.3(2)	75 min.	600°C	10^{10}	10^{12}	10^{12}	>100 *

Table 1: Summary of the results of the experiments on crystal 728. The numbers with asterisks (*) are found from experiment. The other numbers are calculated.

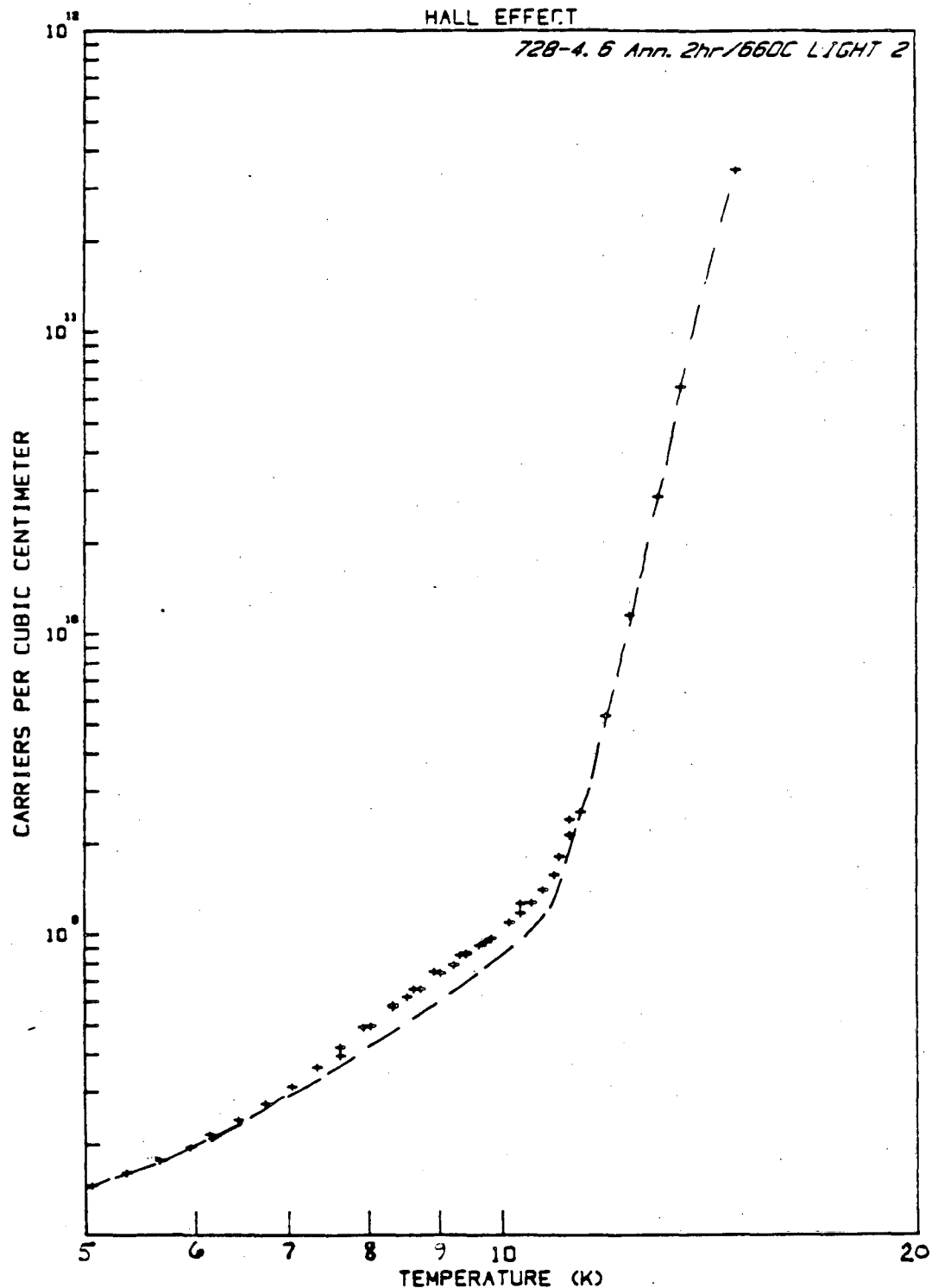


Fig. 17: The free hole concentration when it is dominated by the photoionization of neutral centers in a two level system. The steep portion on the right is due to the freezeout of thermal carriers. The general slope of the curve on the left is caused by the temperature dependence of the recombination coefficient. The dashed line, drawn in, is approximately the character of the curve had there been only one acceptor. The concentration is raised above 8K because the shallow levels become thermally ionized, causing the number of ionized beryllium traps to decrease.

both dark Hall effect and photo Hall effect data so that N_1 , N_2 , E_1 , E_2 , N_D , B_1 and the temperature dependence of B_1 could be found. Since this is quite a large number of fitting parameters, it is best to find a number of them by graphical methods. The value of N_1 can be found quite well with this method. It must also be understood that, when $K_S < 1$, it is impossible to find E_2 since there is no temperature for which the shallow acceptors freeze out.

A method of least squares¹⁸ allows any function of the form

$$0 = F(x,y;c_1, \dots, c_n) \quad (22)$$

to be fit to a set of data. It is obvious that equations 8 and 9 can be put into this form. The method is outlined in Appendix C.

Attempts were made to use this method to fit the charge balance equation to data for the case of the dark Hall effect. Two situations in particular were tried. First is the case where there are essentially just two impurity levels, one donor and one acceptor. This corresponds to the case where $N_D > N_2$. The other case had three impurity levels, one donor and two acceptors with $N_D \ll N_2$. The data distinctly showed the two regimes of half-slope and full-slope freezeout of the shallow level. In both cases, the fitting procedure gave unsatisfactory results. The method was very sensitive to the starting values, and poor starting values (off by a factor of about two) would cause the procedure to diverge. In the case of the three level system, a converging solution fit the donor concentration to the endpoint of the data. Computer generated curves using the results did not match the data. To test the fitting program, some computer simulated data (generated from equations 8 and 9) was used, and the results obtained were good.

There are a number of reasons for the poor performance of this method. First, since the Hall coefficient R_H is equal to r/ne , there is a strong systematic error introduced into the problem. The Hall factor r , is

temperature, field and direction dependent, and attempts to measure or calculate it for holes in germanium have indicated that the approximation $r = 1$ does not hold except for extremely high fields.¹⁹ Since only a field of 1 kGauss was used for these experiments, it is likely that we are introducing a large error in our measurements. As one can see (see figure 15), the temperature dependence of the Hall factor tends to round the curve at higher temperatures.

Two other reasons may be strongly influencing the ability for the function to fit the data. Two assumptions made in the derivation of equations 8 and 9 may not be valid. First, we assumed that there is no effect due to the excited states of the impurities. Blakemore showed that these states can have a strong effect on the temperature dependence of the carrier concentration at high temperatures.²⁰ Furthermore, no attempts were made to account for the double acceptor statistics for the beryllium level. Using such statistics arguments, Schaub, Pensl, and Schulz were able to show that the Hall effect data obtained for Si:Te could not be fitted by single donor statistics,¹⁷ but could be fitted satisfactorily by double donor statistics. Further attempts should be made using double acceptor statistics in curve fitting the data.

No attempts were made to fit the equation to any photo Hall effect data since no success was achieved for dark Hall effect data. It may be possible, once the concentrations and energies are found by graphical methods, to ignore the higher temperature data, where the free hole concentration is completely thermally dominated and the largest errors caused by poor assumptions in the

theory exist, and to fit only the photon dominated region to find N_D , B_{Be} , and the temperature dependence of B_{Be} . Up until now, since we may be creating "hot" carriers caused by high energy radiation ($E \gg E_i$), the temperature dependence of B_{Be} does not show a strict power dependence. Furthermore, N_D , B_{Be} , and the temperature dependence of B_{Be} can be found (as I have done) from graphical methods by plotting the data on a $\log p$ versus $\log T$ graph.

5. CONCLUSIONS

5.1 Summary

The methods used above have shown that when light is used to photoionize free carriers, a population inversion occurs that allows the coefficient for the capture of holes by ionized impurities to be found from the photo Hall effect. Furthermore, once these coefficients are found (by experiments with samples having known values of N_D), this technique can be used to find the concentration of compensating donors N_D .

A further effect, an increase in the lifetime of free carriers due to a decrease in the number of ionized deep acceptors in multilevel systems, was found to exist. This increase in lifetime is characteristic of samples which have very close shallow compensation and explains the high responsivity of photoconductors made with such materials. When $0 < N_D - N_{Sh} \ll N_D$, this increase can be seen from measurements of the photo Hall effect. When $N_D - N_{Sh} < 0$, this increase is not readily visible because of the presence of thermally generated holes in the valence band.

Because the increase in the free hole concentration is proportional to $N_D/(N_D - N_{Sh})$, the photo Hall effect can be used to aid in the characterization of materials which are very closely shallow compensated. Such close compensation of the shallow acceptors is not easily achieved in materials as they are grown.

Curve fitting methods were investigated for the use of analyzing the data. Because the equation determining the free hole concentration is not very accurate, and because of the systematic error introduced by the Hall factor r , the methods did not lead to satisfactory results.

5.2 Suggestions for further study

There are a number of modifications in the experimental method that should be investigated. First, since hot carriers can affect the results of the experiments causing errors in the measurement of the recombination coefficient, some method should be found to eliminate photons of high energies arriving at the sample. This problem can be solved in a number of different ways. The simplest is by means of filters. This method becomes more of a problem of space limitation in the apparatus than anything else. Another possible method is to use a colder black body, e.g. use a heater embedded within the outer radiation shield of the apparatus. This method presents a problem of adding external heat to the system which can make it difficult to attain stability at low temperatures. The last method would be to use a long wavelength laser. Since the apparatus has provisions for optical ports, introducing photons from outside does not present too much of a problem provided that nothing at room temperature interferes with the optical path.

Further investigations into the possibility of curve fitting the data should be carried out. Double acceptor statistics should be investigated as well as the effects of excited states.

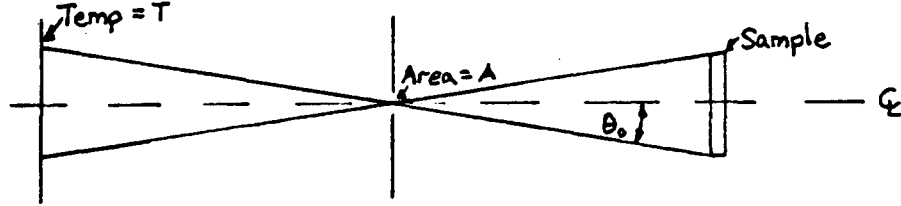
Lastly, all of the studies presented here have only dealt with the beryllium and beryllium-hydrogen centers. Similar studies should be carried out in other systems such as the zinc and zinc-hydrogen systems. Although the step in responsivity has never been seen for photoconductors in Ge:Zn, it is likely that the step occurs at higher temperatures than have been investigated since the ionization energy of the zinc-hydrogen acceptor complex is slightly higher than the shallow levels.

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APPENDIX A
CALCULATION OF PHOTON FLUX

Geometry:



Assumptions:

1. Aperture is small enough so flux is proportional to aperture area.
2. Aperture size is large enough so that diffraction effects do not occur.
3. Sample is approximately circular.

$$u = \frac{8\pi hc^{-3} v^3}{e^{h\nu/kT} - 1} \quad (A1)$$

The energy emitted by a surface at temperature T per solid angle per unit time per unit area per unit frequency is given by

$$e(\nu, \theta, \phi) = \frac{cu \cos \theta}{4\pi} = \frac{2hc^{-2} v^3 \cos \theta}{e^{h\nu/kT} - 1} \quad (A2)$$

The total energy coming into area A within angle θ_0 per unit frequency per unit time is given by the integral over the sample and the aperture:

$$\int_0^{\theta_0} \int_0^{2\pi} A e(\nu, \theta, \phi) \sin \theta \, d\theta \, d\phi = \int_0^{\theta_0} 2\pi A e(\nu, \theta) \sin \theta \, d\theta \quad (A3)$$

The total number of photons of energy greater than $h\nu_0$ per unit time coming through area A within an angle θ_0 is given by dividing (A3) by the energy per photon and integrating:

$$\int_0^{\theta_0} \int_{\nu_0}^{\infty} \frac{2\pi A e(\nu, \theta)}{h\nu} \sin \theta \, d\theta \, d\nu \quad (A4)$$

Evaluation of this integral, by letting $x = h\nu/kT$, yields

$$\int_0^{\theta_0} \int_{x_0}^{\infty} \frac{4\pi c^{-2} v^2 A}{e^{h\nu/kT} - 1} \cos \theta \sin \theta \, d\theta \, d\nu \quad (A5)$$

$$= 4\pi c^{-2} h^{-3} T^3 k^3 A \int_{x_0}^{\infty} \frac{x^2 dx}{e^x - 1} \int_0^{\theta_0} \cos \theta \sin \theta \, d\theta \quad (A6)$$

$$= \pi c^{-2} h^{-3} T^3 k^3 A (1 - \cos 2\theta_0) \int_{x_0}^{\infty} \frac{x^2 dx}{e^x - 1} \quad (A7)$$

$$= (3.16 \times 10^{10} \text{ K}^{-3} \text{ cm}^{-2} \text{ sec}^{-1}) T^3 A (1 - \cos 2\theta_0) \int_{x_0}^{\infty} \frac{x^2 dx}{e^x - 1} \quad (A8)$$

This expression is the total number of photons of energy greater than $h\nu_0$ passing through area A from a surface at temperature T and within an angle θ_0 . Figure A1 plots the integral for a black body at 300K.

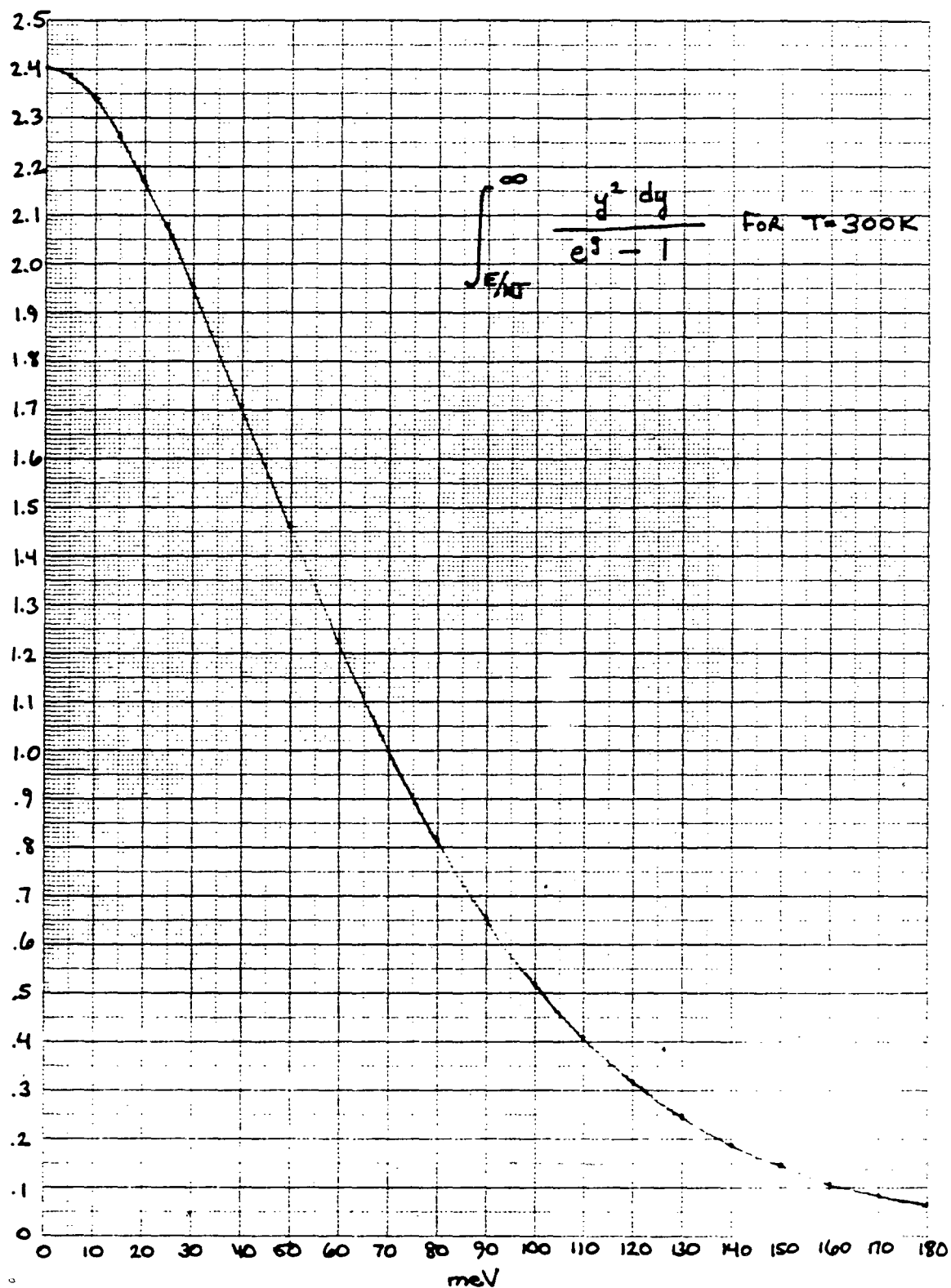


Fig. A1: Graph of the integral in the expression for the flux.

APPENDIX B
APPROXIMATIONS OF THE CHARGE BALANCE EQUATION

The charge balance equation given by equations 8 and 9 for two levels is

$$p + N_D = \frac{N_1}{1 + \frac{4p}{N_V \exp(-E_1/kT) + \frac{\langle \sigma I \rangle_1}{B_1}}} + \frac{N_2}{1 + \frac{4p}{N_V \exp(-E_1/kT) + \frac{\langle \sigma I \rangle_2}{B_2}}} \quad (B1)$$

We wish to find approximation of this equation for different regimes of both the case where the system is in the dark and the case where it is illuminated. In the dark the photo terms $\langle \sigma I \rangle/B$ drop out. In the high temperature regime $\exp(E/kT) = 1$ giving us

$$p + N_D = \frac{N_1}{1 + \frac{4p}{N_V}} + \frac{N_2}{1 + \frac{4p}{N_V}} \quad (B2)$$

In the nondegenerate case, $4p/N_V$ is much smaller than 1, so this expression will be approximately

$$p = N_1 + N_2 - N_D. \quad (B3)$$

In the case $N_D > N_2$, p is much smaller than $N_V \exp(-E_2/kT)$ and so equation B1 becomes

$$p + N_D - N_2 = \frac{N_1}{1 + \frac{4p}{N_V \exp(-E_1/kT)}} \quad (B4)$$

$$= \frac{N_1 N_V}{4p} \exp(-E_1/kT) \quad (B5)$$

When $p \gg N_D - N_2$, then $p(p + N_D - N_2) \approx p^2$, giving us

$$p = \sqrt{\frac{N_1 N_V}{4}} \exp(-E_1/2kT). \quad (B6)$$

When $p \ll N_D - N_2$, then $p(p + N_D - N_2) \approx p(N_D - N_2)$, giving us

$$p \approx \frac{N_1 N_V}{4(N_D - N_2)} \exp(-E_1/kT). \quad (B7)$$

In the low temperature regime when photons are incident on the sample, the exponential term in A1 becomes negligible and the $\langle \sigma I \rangle/B$ term dominates. If we assume that none of the shallow acceptors are photoionized then

$$p + N_D = \frac{N_1}{1 + \frac{4pB_1}{\langle \sigma I \rangle_1}} + \frac{N_2}{1 + \frac{4pB_2}{\langle \sigma I \rangle_2}} \quad (B8)$$

For a sufficiently small flux so that the denominators can be approximated by $4pB/\langle \sigma I \rangle$,

$$p + N_D = \frac{N_1 \langle \sigma I \rangle_1}{4pB_1} + \frac{N_2 \langle \sigma I \rangle_2}{4pB_2}, \quad (B9)$$

$$p = \frac{N_1 \langle \sigma I \rangle_1}{4(p + N_D)B_1} + \frac{N_2 \langle \sigma I \rangle_2}{4(p + N_D)B_2}. \quad (B10)$$

When the shallow acceptors become thermally ionized then

$$p + N_D = \frac{N_1 \langle \sigma I \rangle_1}{4pB_1} + N_2 \quad (B11)$$

$$p \approx \frac{N_1 \langle \sigma I \rangle_1}{4B_1(p + N_D - N_2)} \cdot \quad (B12)$$

APPENDIX C THE METHOD OF LEAST SQUARES

The method outlined by Deming was used to fit the data. This is an outline of the process and does not attempt to prove that the method works. The problem is to find the parameters $c_1, \dots, c_n$ such that the function

$$f(x, y; c_1, \dots, c_n) = 0$$

is a best least squares fit to a set of data x_i, y_i with weights w_{xi} and w_{yi} . The first step is to find the partial derivatives of f with respect to each of the variables. Let f_i be the function f evaluated at x_i, y_i and the c_j 's. Letting $f_{xi} = \partial f / \partial x$, $f_{yi} = \partial f / \partial y$, and $f_{cj} = \partial f / \partial c_j$, each evaluated at x_i and y_i , and if we define L_i to be

$$L_i = f_{xi}f_{xi}/w_{xi} + f_{yi}f_{yi}/w_{yi},$$

then our problem can be put into a problem of solving a system of linear equations. If we start out with some initial guesses c_j , then by solving for the Δc_j in the following equation, we can get a (hopefully) better set of c_j :

$$\begin{bmatrix} \frac{f_{1i}f_{1i}}{L_i} & \frac{f_{1i}f_{2i}}{L_i} & \dots & \frac{f_{1i}f_{ni}}{L_i} \\ \frac{f_{2i}f_{1i}}{L_i} & \frac{f_{2i}f_{2i}}{L_i} & \dots & \frac{f_{2i}f_{ni}}{L_i} \\ \vdots & \vdots & & \vdots \\ \frac{f_{ni}f_{1i}}{L_i} & \frac{f_{ni}f_{2i}}{L_i} & \dots & \frac{f_{ni}f_{ni}}{L_i} \end{bmatrix} \begin{bmatrix} \Delta c_1 \\ \Delta c_2 \\ \vdots \\ \Delta c_n \end{bmatrix} = \begin{bmatrix} \frac{f_{1i}f_i}{L_i} \\ \frac{f_{2i}f_i}{L_i} \\ \vdots \\ \frac{f_{ni}f_i}{L_i} \end{bmatrix}$$

The new c_j are then $c_j - \Delta c_j$. The process is repeated until a given convergence criterion is met.

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