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THE CONTRIBUTION OF PHONON-INDUCED
TUNNELING TO DONOR ESR SPECTRAL
NARROWING IN SEMICONDUCTORS

BY

DAVID LAWRENCE MEIER, 1949-

A THESIS

Presented to the Faculty of the Graduate School of the

UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN PHYSICS

1973

T2863
145 pages
c.1

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ABSTRACT

The narrowing of donor electron spin resonance spectra with increasing donor concentration N_D and increasing temperature T has been observed in semiconductors in the past. One proposed explanation for this phenomenon has been narrowing due to electron motion caused by phonon-induced tunneling (hopping) between donor sites. According to the Anderson narrowing theory, the line width of the narrowed line can be expressed in terms of the average square spread of the non-narrowed spectrum, $\langle H^2 \rangle_{ave}$, and the average frequency of electron motion, ω_h . Previous work has been done on narrowing by hopping, but rigorous expressions for ω_h or $\langle H^2 \rangle_{ave}$ have never been derived. In addition, the past treatment has omitted several important concepts from the problem which have a direct bearing on the theoretical results.

To rigorously examine if the hopping process was producing the spectrum, it was first necessary to derive expressions for ω_h and $\langle H^2 \rangle_{ave}$. To find the average hopping frequency, a previous derivation of the transition rate for hopping was averaged over the electron ensemble and the donor and acceptor impurity ensemble with methods derived in the hopping theory for electrical conductivity in a semiconductor containing impurities. These methods had not been applied to narrowing in the past. A major portion of this derivation was the discussion and calculation of the Fermi energy for electrons in donor ground states, ζ_g , based, in part, on a previous treatment of this quantity. To complete the calculation, analytical and numerical solutions for ω_h and ζ_g were derived. The

resulting ω_h was found to be a function of N_D and T . It was also found to be a function of the compensation K , the ratio of the acceptor concentration to the donor concentration. This K dependence had not been previously predicted, and the N_D and T dependences were in disagreement with what earlier treatments had supposed. To calculate $\langle H^2 \rangle_{ave}$, a mathematical distribution function describing the shape of the non-narrowed donor ESR spectrum was deduced and the square of the spread of the spectrum was subsequently averaged over that distribution. This result also disagreed with previous expressions for $\langle H^2 \rangle_{ave}$.

The new narrowing theory was then compared with existing published data. It was found that hopping could not predict the observed N_D dependence of the line width and could not predict all of observed T dependence. Thus it was concluded that hopping is not the only mechanism causing narrowing and is, in fact, not the dominant mechanism. Complete rejection of phonon-induced tunneling as a contributing mechanism was not possible, however. This was due partly to the lack of data on the direct K dependence of the line width and partly to the lack of data on the influence of compensation on the temperature dependence of the line width. Thus, an experiment was proposed to obtain the necessary data on the K and T dependences to decide conclusively whether or not hopping contributes to donor ESR spectral narrowing.

ACKNOWLEDGEMENTS

I would like to express my appreciation to Dr. Edward B. Hale, Professor of Physics, for suggesting this problem, for his helpful guidance, for his invaluable advice in the preparation of this thesis, and for his efforts leading to the presentation of this work as a paper at the March, 1973 meeting of the American Physical Society. I would also like to thank those others whose assistance contributed greatly to the completion of the work: Dr. William F. Parks, Professor of Physics, who gave many hours of his time to discussion of the details of the problem; Dr. James J. Higgins who have helpful advice on statistical aspects of the work; Mr. Robert Sawyer whose preliminary work on the problem helped bring it to a speedier conclusion; and Mrs. Carol Rodman whose expert typing resulted in a very neat and accurate manuscript.

In addition, I would like to thank all those who contributed directly or indirectly to the support of this work: the Department of Health, Education, and Welfare; the Air Force Office of Scientific Research; the UMR Physics Department; the Air Force Reserve Officer Training Corps; and the Phelps County Memorial Hospital.

Furthermore, I would like to express my appreciation to all those who were patient and understanding to release me from other responsibilities in order that this work might be completed: Colonel Madison M. Daily, Major Lee O. Cunningham, and Major James W. Clinton, U.S. Air Force; my parents, Mr. and Mrs. Lawrence Meier;

and those of my wife, Mr. and Mrs. Clarence A. Schoonover; and the active and alumni brothers of Beta Sigma Psi Fraternity.

Finally, I would like to express the deepest gratitude to my wife, Ann. Throughout the past two years she has worked untiringly to further my graduate education and has offered nothing but encouragement, understanding, and love. This thesis is dedicated to her.

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I. INTRODUCTION

Electron spin resonance (ESR) experiments on isolated donor impurities in lightly doped silicon¹⁻³ and germanium^{4,5} have yielded valuable information concerning the wave function of the donor electron as well as its spin interactions with the donor nucleus and the surrounding semiconductor nuclei. Additional experiments⁴⁻¹³ on more heavily doped samples have indicated that the ESR spectrum may also hold clues to the interactions between the donors themselves. In particular, it has been found that at donor concentrations where the wave functions from neighboring donor electrons begin to overlap, the hyperfine structure indicative of isolated donors becomes unresolved and a single narrow line appears instead. However, before the full potential of these latter experiments can be realized, a deeper understanding is needed of the various interactions between the donor electrons and their effects upon the ESR spectra. This thesis will deal primarily with the particular interaction called phonon-induced tunneling or hopping. This phenomenon is the means by which an electron localized on one donor may make a transition to another with the assist of a lattice phonon. The discussion will study the mechanism of hopping itself, determine how it should narrow the ESR spectrum of donor electrons, and compare the findings with experiment.

A. THE OBSERVATION AND THE THEORY OF ESR SPECTRAL NARROWING

In order to study the influence of hopping on the ESR spectrum of a donor electron, the nature of the observed spectrum itself and the

methods of altering that spectrum must be explored. A typical ESR spectrum of donor electrons for low donor concentrations consists of $2I+1$ Gaussian lines, where I is the spin of the donor nucleus. The distinct lines themselves arise from the Fermi contact interaction of various electrons with the donor nucleus. The Gaussian line shape is due to the Fermi contact and dipole-dipole interactions with the surrounding silicon or germanium nuclei. Figure 1(a) shows the derivative of such a spectrum with respect to the magnetic field, the form in which the spectrum is normally recorded by experimentalists.

For these donor electrons the spin state may be written as

$$\psi_{\text{spin}} = |m_s \ m_I \ m'\rangle , \quad (1)$$

where m_s is the spin quantum number of the electron itself, m_I is the spin state of the donor nucleus, and m' represents the composite spin state produced by the interactions of the electron with the surrounding semiconductor nuclei. It can be shown that the effect of the latter interactions is to broaden each of the $2I+1$ lines, which accounts for the Gaussian line shape.

Moreover, an electron contributes to the spectrum only if it is in the donor ground state. It must be in the ground state because the major Fermi contact interaction, the one that produces the $2I+1$ lines, occurs only for electrons in a S state^{1,4} and is observed only at very low temperatures. It is thus assumed in the theory which shall be used for hopping in the next section that electrons are only in the ground state.

Figure 1. The ESR spectrum of arsenic-doped germanium for various concentrations of the arsenic impurity. $T = 4.2 \text{ }^\circ\text{K}$; magnetic field parallel to $[100]$ axis. Data from Reference 12, Figure 1.

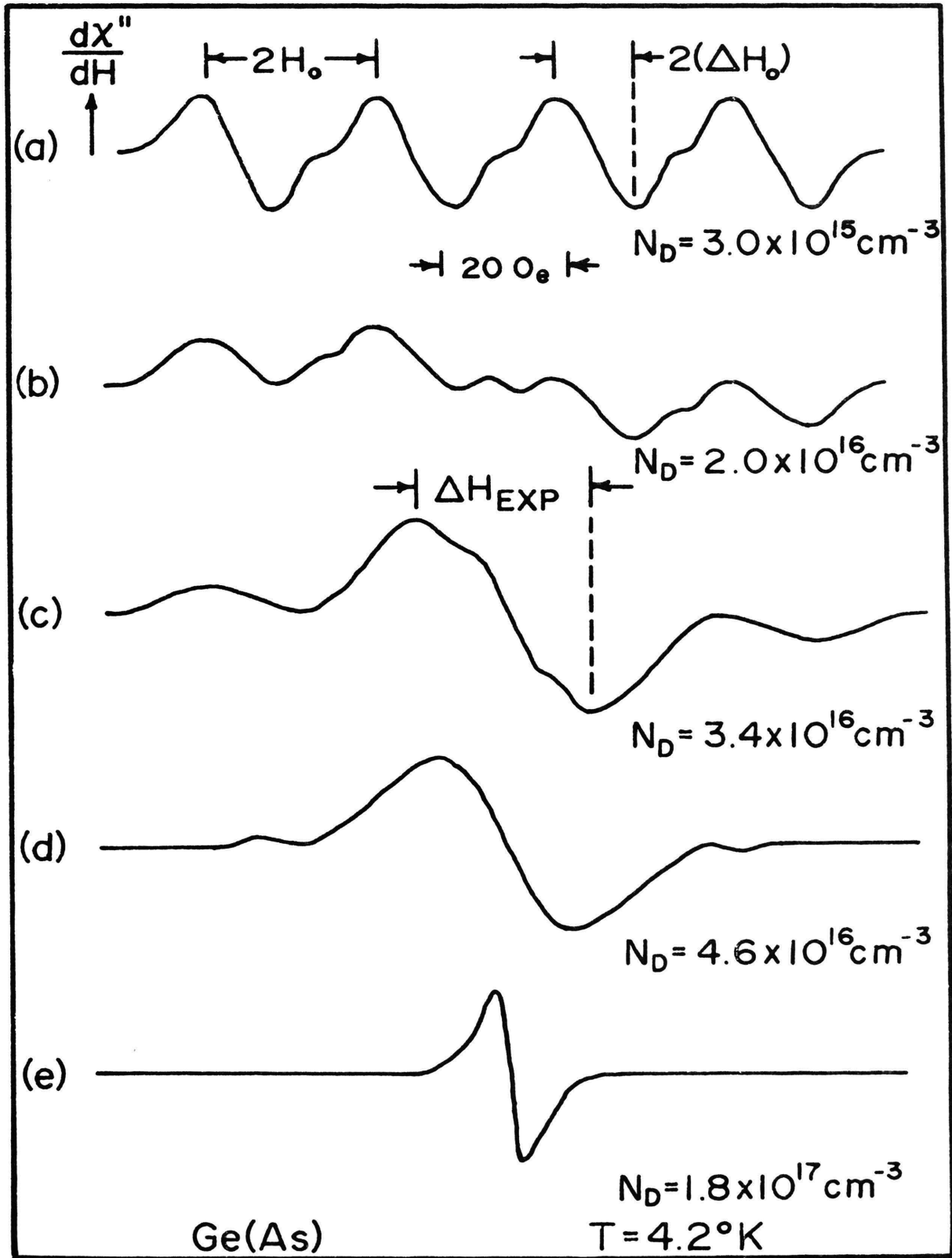


Figure 1

The well defined 2I+1 line spectrum is observed only at donor concentrations where the electron can be considered localized on the donor (below $2 \times 10^{16} \text{ cm}^{-3}$ in silicon and $5 \times 10^{15} \text{ cm}^{-3}$ in germanium). For fixed temperatures, when the donor concentration is increased, the 2I+1 hyperfine lines begin to reduce in intensity and a single line starts to appear in the center of the spectrum. As the concentration is further increased, this center line increases in intensity and finally dominates the spectrum at high concentrations (see Figure 1). The most interesting property of this line is that it grows narrower with increasing donor concentration and narrows even further with increasing temperature (see Figure 2).

Bloembergen, Purcell, and Pound¹⁴ predicted that such narrowing could be achieved if the motion of the spin particles (donor electrons in this case) between various spin states were rapid enough. In the case of the donor electron, those transitions contributing to the narrowing would be ones where $\Delta m_I \neq 0$ and/or $\Delta m' \neq 0$. The transitions where $\Delta m_S = \pm 1$ are the ones which cause the ESR signal and do not contribute to the actual narrowing of the line. Hereafter in this thesis, when the phrase "motion between spin states" is used, it will refer to the former transitions and not those with $\Delta m_S = \pm 1$.

Anderson¹⁶ performed a detailed study of this motional narrowing process and found that a single line should be observed and the breadth (half-width at half-max) of this line should be (see Appendix B for more discussion)

Figure 2. The ESR spectrum of arsenic-doped germanium for various temperatures. $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$; magnetic field parallel to the [100] axis. Drawn to fit linewidth data in Reference 12, Figure 3.

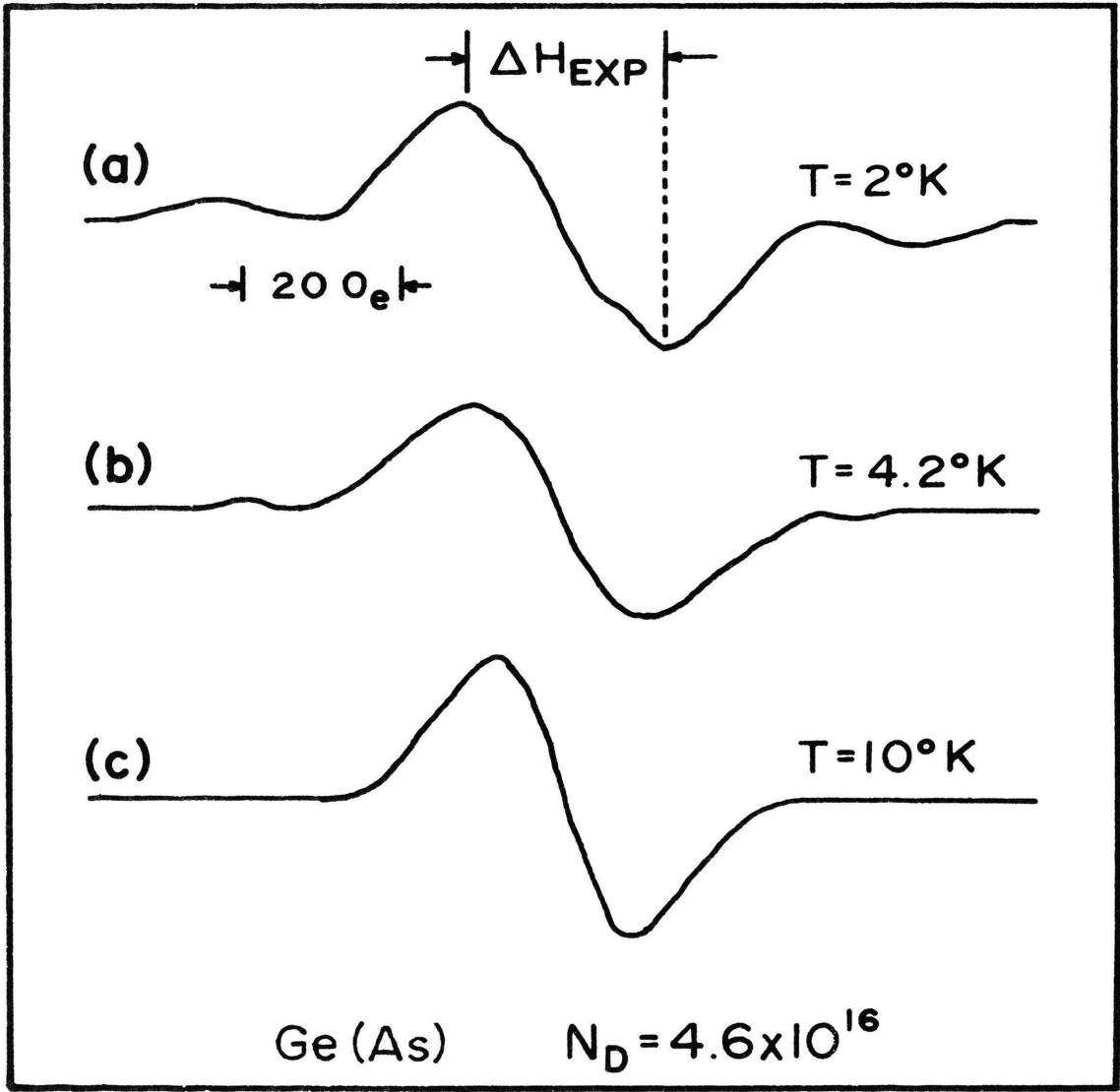


Figure 2

$$\Delta\omega = \frac{\langle\omega^2\rangle_{\text{ave}}}{\omega_h} \quad (2)$$

if

$$\omega_h \gg [\langle\omega^2\rangle_{\text{ave}}]^{1/2} ,$$

where $\langle\omega^2\rangle_{\text{ave}}$ is the average square spread of the non-narrowed spectrum from its center and ω_h is the average transition rate or hopping rate of the spin particle between the various spin states. Since, however, most measurements are made in terms of the magnetic field, a more useful form for Equation (2) (for electrons) can be written as:

$$\Delta H = \frac{g\mu_B \langle H^2 \rangle_{\text{ave}}}{\hbar\omega_h} \quad (3)$$

with the rapid motion condition now given by

$$\omega_h \gg \frac{g\mu_B [\langle H^2 \rangle_{\text{ave}}]^{1/2}}{\hbar} ,$$

where ΔH is the breadth of the resonance line in magnetic field, g is the Lande g factor for the donor electron, μ_B is the Bohr magneton, and $\langle H^2 \rangle_{\text{ave}}$ is the mean square spread of the non-narrowed spectrum from its center expressed in magnetic field units. If Equation (3) is valid, i.e., if the motion of the donor electrons between the many spin states is rapid enough, then the $2I+1$ ESR lines will not be observed and instead a single line of width ΔH will be seen.

Motional narrowing thus appears as a possible mechanism for explaining the aforementioned experimental ESR spectra. However, it is to do so, a physical process must be found which causes motion of the donor electrons between the many spin states. Moreover, since Equation (3) shows that the theoretical line breadth decreases as the rate of motion increases, this narrowing process must increase the rate of motion of the electrons with increasing donor concentration and with increasing temperature, in order to conform with observation.

B. PHONON-INDUCED TUNNELING AS A NARROWING MECHANISM

Since phonon-induced tunneling causes physical motion of the donor electron, the possibility exists that hopping can cause motion between the spin states and hence can narrow the donor ESR spectrum. The theoretical model of phonon-induced tunneling should therefore be examined and related to these resonant states. The particular model presented here is due to Miller and Abrahams^{17b,c} whose theory on conduction of electrons by hopping has explained the resistivity of semiconductors containing impurities.¹⁷

The crystal in the model is a group IV semiconductor (Si or Ge) having dielectric constant k_0 and doped with an n-type atom (donor) that is located at substitutional site within the lattice. Acceptors are also assumed to be present in the crystal. While the donors and acceptors are considered randomly distributed, it is assumed that over a large volume the average concentration N_D or N_A is constant. In addition, the concentration of the acceptors is less than that of the donors; hence, N_A donors have lost their electrons to acceptors

while $N_D - N_A$ are still occupied. The situation is characterized by a compensation ratio $K = N_A / N_D < 1$.

In Figure 3 two typical potential wells, at an occupied (i) donor and a vacant (j) donor, are illustrated along with their energy states (not to scale). These levels, given to first order by the effective mass theory, have been altered by a random perturbation. In the present model the perturbing mechanism is the coulomb field of a nearby acceptor. With the unperturbed ground state taken to be $E=0$, the magnitude of the perturbation at i, E_i , gives the energy of the i^{th} ground state donor electron. Since the perturbation may affect one site more strongly than the other, the i and j ground states may differ by an energy $\Delta_{ij} = E_i - E_j$. As long as Δ_{ij} is large compared to the energy of overlap between i and j (see Appendix A for a better definition of the overlap energy), the states on i and j are localized. In addition, if the electron is in the ground state, it is also localized in one of the spin states which produce the ESR spectrum in Figure 1(a). If the above conditions are met and no other perturbation act upon the system, it tends to remain in the state with one electron on i and none on j.

If a phonon arrives at i, however, and has an energy Δ_{ij} , there is a finite probability per unit time U_{ij} that j may become occupied by the electron previously localized on i. Furthermore, the Fermi contact interaction after the transition may be different from that before as signified by the change in orientation of the nuclear spin vector in Figure 3. That is, the motional or hopping process can

Figure 3. Schematic diagram of the phonon-induced tunneling process, Miller and Abraham theory.^{17b} Phonon must have energy $\Delta_{ij} = E_i - E_j$ to cause transition. Note that the Fermi contact interactions may change upon transition, signified by the change in orientation of donor atom spin states m_I . Hence hopping can change the spin state.

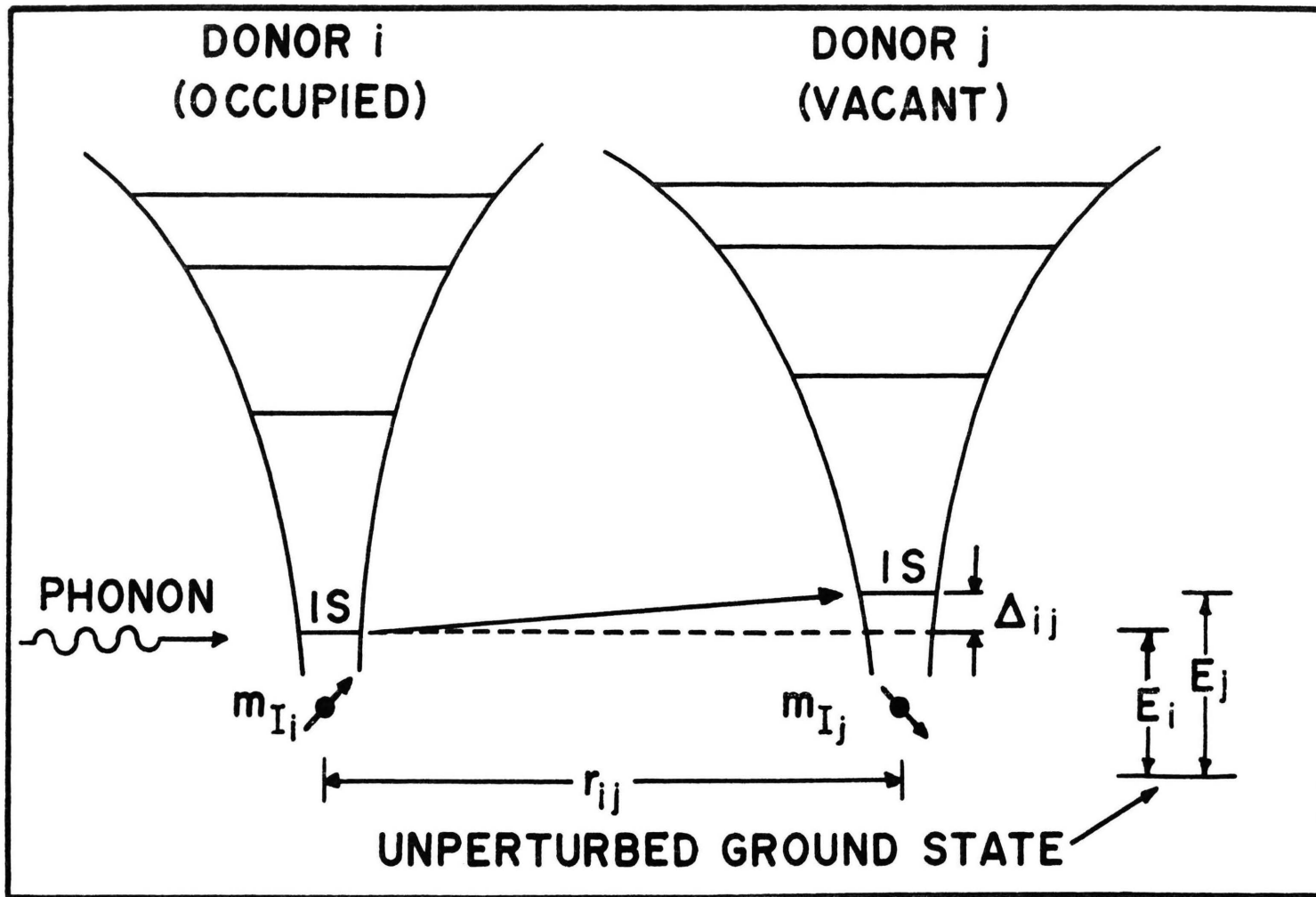


Figure 3

cause changes in the spin states. Therefore, according to the Anderson theory a series of these transitions between ground states should cause the ESR spectrum to narrow. Hopping is thus a narrowing process. Furthermore, the average transition rate for hopping ω_h should be related to U_{ij} and a corresponding line breadth should be calculable from Equation (3).

Hopping also has two important physical properties. First, since it involves a phonon, the probability of a transition should increase with temperature. Second, since this transition probability should increase as the donors are brought closer together (see Section II), it should also increase with donor concentration. Thus from a qualitative point of view, phonon-induced tunneling seems a likely candidate to explain the observed narrowing of the donor ESR spectrum.

The idea is not new. Several others have attempted to treat the problem of motional narrowing by hopping. Their work and their results are discussed in Section II. However, as is noted there, most of their conclusions are based upon incorrect expressions for both ω_h and $\langle H^2 \rangle_{ave}$. In particular, ω_h has not been averaged properly over the donor electron ensemble and the impurity ensemble. Section III is concerned with this averaging process. The definition of ω_h and the model for averaging is presented in Part A of Section III. In Part B the electron statistics are discussed and the Fermi energy for ground state electrons is calculated. Part C discusses the distribution of the impurities and how it affects the average hopping frequency mathematically. In Part D the results of the

previous parts in Section III are combined to arrive at a formal solution for ω_h . Part E then approximates the formal solution in the region of low compensation and approximates further in various regions of temperature. The calculation of ω_h is finally concluded with a discussion in Part F of the results of computer and analytic calculations of the average hopping frequency. Next, Section IV gives a brief calculation of the correct expression for $\langle H^2 \rangle_{\text{ave}}$ and thus completes the theoretical portion of the thesis.

In Section V, Part A, the theory is compared with the theories of previous authors. Part B of Section V compares the theory of narrowing by hopping and draws conclusions on the possibility that such a narrowing process is being observed experimentally. Part C proposes an experiment to clear up any uncertainty remaining because of the lack of data on the K dependence of the line width. Finally Section VI summarizes the findings and conclusions of this work. In Appendix A the mathematics of the Miller and Abrahams model is discussed and the transition rate U_{ij} for the hopping process is briefly rederived. Appendix B integrates the hopping process into the formalism of the Anderson narrowing theory and mathematically justifies phonon-induced tunneling as a narrowing mechanism. Appendix C deals with computer programs used in the calculation of the Fermi energy and the average ω_h .

II. REVIEW AND CRITIQUE OF PREVIOUS WORK ON PHONON-INDUCED TUNNELING AS A NARROWING PROCESS

Motion of donor electrons was initially recognized as a possible narrowing mechanism by Feher, Wilson, and Gere.⁶ Several authors have since attempted to apply the theory of hopping to explain the observed ESR line narrowing in a quantitative manner. The first to do so was Wilson.⁴ He combined the Anderson formulation, Equation (3), with the Miller and Abrahams phonon-assisted tunneling transition rate between an occupied and an unoccupied donor. This transition rate (Equations II-14 and II-19 of Reference 17b) is

$$U_{ij} = \frac{1}{B} r_{ij}^{3/2} \exp(-2r_{ij}/a) \begin{cases} \frac{|\Delta_{ij}|}{\exp(\beta|\Delta_{ij}|)-1} & \text{phonon absorption} \\ & (\Delta_{ij} < 0) \\ \frac{\Delta_{ij}}{1-\exp(-\beta\Delta_{ij})} & \text{phonon emission} \\ & (\Delta_{ij} > 0) \end{cases} \quad (4)$$

Here r_{in} is the distance between the i and j nuclei, a is the transverse radius of the envelope function for a single donor valley, Δ_{ij} is as defined earlier (see Figure 3), and $1/B$ is a series of constants given in Appendix A. Wilson inserted

$$r_{ij} = R_D = (3/4\pi N_D)^{1/3} \quad \text{and} \quad \Delta_{ij} = \Delta \quad (\text{an arbitrary constant}) \quad (5)$$

into Equation (4), set $U_{ij}(R_D, \Delta) = \omega_h$, and with Equation (3) obtained

$$\Delta H = \frac{g \mu_B B(\Delta H_{hfs}^2)}{\hbar} R_D^{-3/2} \exp(2R_D/a) \begin{cases} \frac{\exp(\beta|\Delta|)-1}{|\Delta|} \\ \frac{1-\exp(-\beta\Delta)}{\Delta} \end{cases} \quad (6a)$$

or

$$\Delta H = \frac{g \mu_B B(\Delta H_{hfs}^2)}{\hbar} R_D^{-3/2} \exp(2R_D/a) \frac{[1-\exp(-\beta\Delta)]}{\Delta} \quad (6b)$$

for all Δ . Note that for $\langle H^2 \rangle_{ave}$ he used the square of ΔH_{hfs} , defined as the entire spread of the non-narrowed spectrum measured from the center of the first line on the left (see Figure 1) to the center of the last line on the right. Figure 4(a) shows a plot of Wilson's data on the experimental line width (ΔH_{EXP}), measured between the inflection points of the narrowed spin resonance spectrum, for phosphorus and arsenic-doped germanium. The figure shows that the line width does indeed increase exponentially with R_D as Equation (6) suggests, but that the slopes of the lines give $a = 100 \text{ \AA}$ for arsenic and $a = 260 \text{ \AA}$ for phosphorus, which are much larger than the effective mass values of 60 \AA and 70 \AA , respectively. Wilson's data on the temperature dependence of ΔH_{EXP} consists of only two points for each N_D and hence are not enough for analysis of the T dependence of Equation (6). Before discussing Wilson's calculational methods in detail, one should consider the results of other authors who essentially used the same equation as Wilson, namely, Equation (6).

Figure 4. The experimentally observed R_D dependence and temperature dependence of ΔH_{EXP} . Data on the R_D dependence (a) was taken from Reference 4. Data on the T dependence was taken from Reference 5.

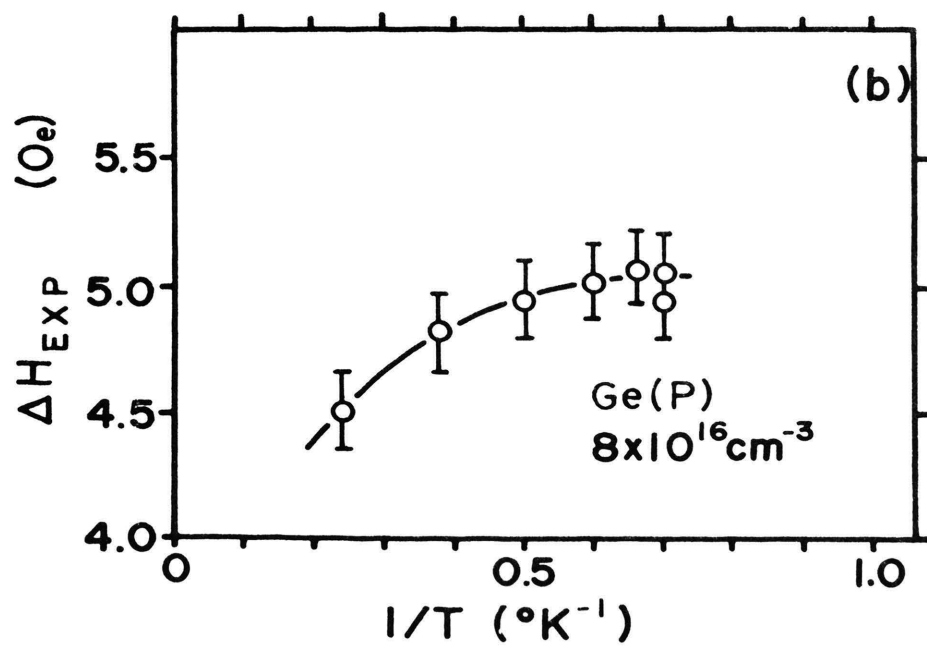
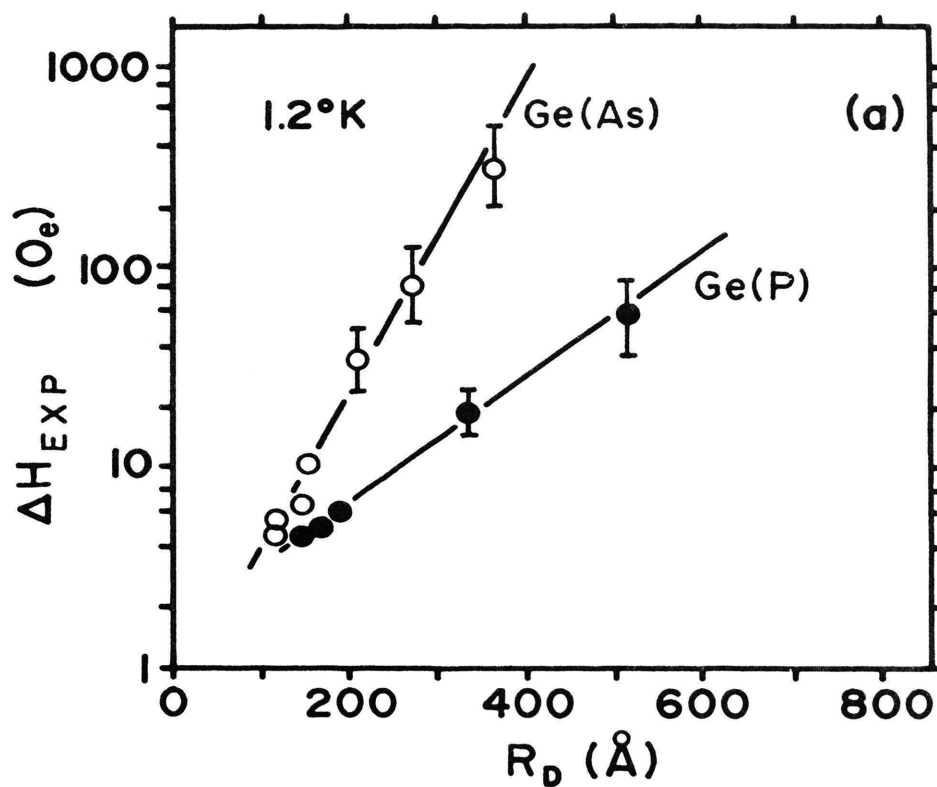


Figure 4

Morigaki and Mitsuma⁵ obtained several points on the T dependence of ΔH_{EXP} for phosphorus-doped germanium (see Figure 4(b)). Upon comparing Equation (6) to their data, they concluded that the temperature dependence as well as the donor concentration dependence of the observed ΔH_{EXP} could be explained by hopping. That is, they believed their data on ΔH_{EXP} in Figure 4(b) was proportional to $[1-\exp(-\beta\Delta)]$ with the value of Δ needed to fit the data lying between 0.34 meV and 0.54 meV.

However, this fairly good agreement of Equation (6) with experiment as found by these authors is misleading. Several assumptions made in the derivation of Equation (6) are responsible for the qualitative agreement of Equation (6) with experiment. One may summarize the questions concerning these assumptions as follows:

1. a) U_{ij} was derived for a single pair of donors, one occupied and one vacant (see Appendix A). However, the Anderson narrowing theory requires ω_h in Equation (3) to be an average frequency of transition per electron. It is not appropriate to insert $r_{ij} = R_D$ into Equation (4) to find this average as is shown briefly in this section and more completely in Section III. In fact, an exponential dependence on R_D is not expected.
- b) Insertion of R_D , the average distance between donors, implies that hopping between only nearest neighboring donors is considered. Tunneling to more distant donors, however, is also significant as shown in Section III.

2. The distribution of the $N_D - N_A$ electrons on the N_D donors has not been taken into account. For example, the donor j is assumed empty and there is no dependence in Equation (6) which takes into account the compensating acceptor. The distribution of electrons will be shown in Section III to have a strong dependence upon the compensation and the temperature.
3. The parameter Δ_{ij} , the energy difference between two sites, clearly has no unique value, such as Δ , for various pairs of donors. Some sort of averaging process over the possible values of Δ is needed. Hence, as is shown in Sections III and V, the final result for ΔH will not even contain functions of such a microscopic parameter.
4. The expression ΔH_{hfs}^2 is not the same quantity as $\langle H^2 \rangle_{ave}$ of the Anderson theory and ΔH_{EXP} is not precisely the line breadth ΔH . The confusion over these parameters is discussed in detail in Sections IV and V.

The paragraphs below discuss each of these four points and the need for new theoretical calculations of the influence of hopping on the donor ESR spectral narrowing.

First of all, the Anderson narrowing theory requires that an average ω_h per electron be inserted into Equation (3) to find the line breadth. However U_{ij} is not an average. It represents only the microscopic transition rate between two donors. An average of U_{ij} over the microscopic parameters r_{ij} and Δ_{ij} can be written as

$$\bar{U} = \int dr_{ij} f(r_{ij}) \int d\Delta_{ij} G(\Delta_{ij}) U_{ij}(r_{ij}, \Delta_{ij}) \quad , \quad (7)$$

where $f(r_{ij})$ and $G(\Delta_{ij})$ are appropriate probability distributions for r_{ij} and Δ_{ij} . It thus appears that the average U in Equation (7) can be of the same form as $U_{ij}(R_D, \Delta)$, the expression used in Equation (6), only if the functions $f(r_{ij})$ and $G(\Delta_{ij})$ are sharply peaked at the values R_D and Δ , respectively.

However, in a randomly ordered distribution, such as the distribution of donors in a semiconductor, one cannot usually consider the probability that two donors are separated by a distance r_{ij} to be sharply peaked at one value. Hence one should investigate when this can be done in Equation (7). (The similar question about Δ_{ij} and its implications will be discussed later.) The criterion for $f(r_{ij})$ being sharply peaked with respect to r_{ij} is that the width of this function be much smaller than the width of $U_{ij}(r_{ij})$. If, as usually done, a Poisson distribution of nearest neighbors is assumed, then the expression for $f(r_{ij})$ is^{17b}

$$f_1(r_{ij}) = \frac{3r_{ij}^2}{R_D^3} \exp[-(r_{ij}/R_D)^3] \quad , \quad (8a)$$

where the subscript one denotes nearest neighbors. The width at half-max of this function is about $0.83 R_D$. And the width of the r_{ij} dependent part of $U_{ij} \propto r_{ij}^{3/2} \exp(-2r_{ij}/a)$ is about $1.54 a$. The criterion for $f_1(r_{ij})$ being sharply peaked is then

$$0.83 R_D \ll 1.54 a$$

or

$$\frac{3.7}{a^3} \times 10^{-2} \ll N_D . \quad (8b)$$

For germanium Equation (8b) yields $N_D \gg 1.6 \times 10^{17} \text{ cm}^{-3}$ and for silicon $N_D \gg 4.6 \times 10^{18} \text{ cm}^{-3}$. At these concentrations, however, the wave functions cannot be considered localized and the derivation leading to U_{ij} (see Appendix A) is no longer valid. Thus inserting R_D for r_{ij} is not a good method for averaging U_{ij} .

Another problem with using Equation (6) is that only nearest neighbors are taken into account. In fact, transitions to other than nearest neighbors are also significant and should be considered. For example, a distribution similar to Equation (8a) can be written for next nearest neighbors:

$$f_2(r_{ij}) = \frac{3r_{ij}^5}{R_D^6} \exp[-(r_{ij}/R_D)^3] . \quad (9)$$

The average nearest neighbor is actually at $0.89 R_D$ (not R_D), according to Equation (8a), and the average next nearest neighboring donor is at $1.19 R_D$ from Equation (9). The ratio of the transition rate for donors separated by $0.89 R_D$ to that for a separation of $1.19 R_D$ is about $\exp(-0.60R_D/a)$ from Equation (4). For concentrations around $2 \times 10^{16} \text{ cm}^{-3}$ in Ge and $5.3 \times 10^{17} \text{ cm}^{-3}$ in Si, this factor is 10% and even greater for higher concentrations. Since these are concentrations for which narrowing occurs, it can be seen that

nearest neighbors cannot be neglected in motional narrowing by hopping. It appears that U_{ij} should have been averaged over the geometrical distribution of donors in a more accurate manner.

There is, however, another important idea completely unexpressed by Equation (6). Donors i and j were assumed to be occupied and unoccupied, respectively. This effectively means that a compensation ratio of $K = 0.5$ was assumed. However, in most of the samples examined to date K is around 1% or less. The lack of K dependence in Equation (6) seems to indicate that the influence of acceptors on the statistics of how electrons are distributed on the donors has not been considered. Furthermore, since this distribution should be affected by temperature, an important temperature dependent factor seems to be lacking in Equation (6) as well. In the Miller and Abrahams^{17b} theory of impurity conduction, the electron distribution, density of states, and the coulomb repulsion of nearby acceptors were all taken into account, as well as how such an electron distribution was affected by temperature. The success of their theory is due to this treatment and due to the ensemble averaging of an expression similar to Equation (4). If one desires to apply their theory of hopping to the ESR line narrowing problem, one should use the entire theory, including the electron statistics as well as the methods of averaging over the impurity ensemble. These techniques have not been employed in any narrowing calculations previous to this thesis.

The apparent agreement in the temperature dependence of Morigaki and Mitsuma's⁵ data with Equation (6) is as misleading as the previous

"agreement" with the donor concentration dependence. Since the distribution of acceptors is random, the perturbation upon the ground states is also random. Hence Δ_{ij} must also be described by a distribution. Indeed, in the Miller and Abrahams treatment^{17b} $G(\Delta_{ij})$ was considered to be sharply peaked, but at the value $\Delta_{ij} = 0$, not at the positive constant Morigaki and Mitsuma needed to fit the data.

Furthermore the positive Δ was chosen because when inserted into Equation (6), it produces a curve which approaches a constant as T approaches zero, while a curve with $\Delta < 0$ would approach infinity. But the observation that the line width data approaches a constant as T approaches zero does not even correspond to phonon emission when account is taken of the distribution of electrons upon donors. This occurs because as the temperature approaches zero, phonons are emitted until the vacant donors are those which are as close as possible to a negatively ionized acceptor. Then no more emission can occur. Thus, the probability of a transition approaches zero as T approaches zero. This effect, due to the T dependence of the electron distribution, is discussed in greater detail in the new derivation of ω_h in Section III. The expression for ΔH should thus approach infinity as T goes to zero for the case of emission or absorption. (Actually, since Equation (3) is not valid if the hopping frequency is low enough, the data should show that the spectrum reverts to its normal form, not an infinite line width.) The fact that the line width remains narrow and approaches a constant width as T approaches zero is the first hint that phonon-induced tunneling

cannot be the only narrowing process occurring at these temperatures and concentrations. This conclusion is contrary to the suggestions of Wilson and Morigaki and Mitsuma.

Finally there is a question on the substitution of ΔH_{hfs}^2 for $\langle H^2 \rangle_{\text{ave}}$ in Equation (6), since ΔH_{hfs}^2 is the square of the entire spectral spread, while $\langle H^2 \rangle_{\text{ave}}$ is stated by Anderson to be the average square spread from the center of the spectrum. As will be seen in Section IV, the use of ΔH_{hfs}^2 yields line breadths about one order of magnitude too high. In addition it seems that to be strictly quantitative, the Lorentzian line breadth (half-width at half-max) should be related to the Lorentzian line width ΔH_{EXP} . This relation is found in Section V to be $\Delta H_{\text{EXP}} = 2 \Delta H / \sqrt{3}$.

Other experimentalists⁷⁻⁹ applied the incorrect Equation (6) to similar results in silicon. The next major addition to the motional narrowing theory was from Zhurkin, Penin, and Prem Swarup¹⁰. They inserted the Miller and Abrahams activation energy for phonon-induced impurity conduction^{17b} ϵ_3 for Δ_{ij} , retained R_D for r_{ij} in the absorption part of Equation (4), and used the resulting $U_{ij}(R_D - \epsilon_3)$ as the averaged transition probability for hopping. This is also questionable. The ϵ_3 activation energy for hopping conduction was a direct result of the electron statistics for the system of donor electrons which, as noted earlier, have been left out of Equation (4). Impurity conduction theory^{17b} states that for low compensations

$$\epsilon_3 = \zeta_g - 1.35 E_A \quad , \quad (10a)$$

where ζ_g , the Fermi energy of the donor ground states, and E_A are given by

$$\zeta_g = E_D = \frac{e^2}{k_o R_D}$$

and

$$E_A = \frac{e^2}{k_o R_A} \quad , \quad \text{where} \quad R_A = \left(\frac{3}{4\pi N_A} \right)^{1/3} . \quad (10b)$$

The interpretation of why Equation (10a) gives the activation energy for impurity conduction (taken in part from Reference 17a) is as follows. For low compensations the charge carriers are the positively charged hole at the vacant donor sites. During conduction they travel from donor to donor with the assist of a phonon. Although this type of conduction is not entirely free, one might term it as "quasi-free" if the phonon energies needed for transition Δ_{ij} are small enough to be attained by phonons available in large quantities at relatively low temperatures. Now the acceptors, imbedded in this sea of donors, alter the donor ground states with their coulomb potentials. As a result the positive carrier has a lower energy nearer the negative acceptor and a higher energy farther away. (The case for the electron carriers is just the reverse.) In addition, because the coulomb field is more intense near the acceptor, the Δ_{ij} energies are on the average greater nearby an acceptor than farther away from it. As far as the carrier is concerned, then, the region close to an acceptor is like a "bound

state" because of the higher Δ_{ij} 's while the region far from an acceptor allows quasi-free conduction because the Δ_{ij} 's are smaller.

Therefore at very low temperatures, before the carrier can contribute to conduction, it must be excited from its lowest state near an acceptor to one which is far from the acceptor so that quasi-free conduction takes place. In the Miller and Abrahams theory, the former state is effectively at a distance R_D from the acceptor, while the latter is effectively at a distance $R_A/1.35$ from the acceptor. Hence, the energy of the excitation for conduction is about $e^2/k_0 R_D - 1.35e^2/k_0 R_A$.

One must note, however, that this excitation is not attained by a single hop but consists of many hops of the carrier from a donor close to the acceptor to donors successively farther away. Thus ϵ_3 is not one Δ_{ij} but the sum of many Δ_{ij} 's. It cannot, therefore, be equated with an average Δ , as Zhurkin, et al., have done. If an average Δ did exist, it would be much smaller than ϵ_3 .

The most recent authors to study the idea of narrowing by hopping were Gershenzon, Pevin, and Fogel'son^{12,13}. They concluded that electron motion produced by any impurity conduction process (including hopping) was not an effective narrowing mechanism for two reasons. The first reason was obtained by assuming that the $T = 0$ intercept of the data was due to the temperature independent exchange narrowing phenomenon. (The concept of exchange narrowing is too involved to be discussed here. A brief discussion, however, is given in Section V.) Then they tested the hypothesis that electron

motion produced the temperature dependent part of the line width over and above the $T = 0$ exchange narrowed part by using their theory (discussed below) of how electron motion is activated by phonons. Comparing this theory with their data, Gershenzon, et al., concluded that electron motion did not predict the proper temperature dependence of narrowing. The second reason for rejecting electron motion was obtained by noting that the compensation dependence in the narrowing in one sample was exactly opposite to what one would expect intuitively from impurity conduction. In the next few paragraphs the former reason is discussed in greater detail and critiqued. While the latter reason is explained in greater detail below, it is more appropriate to defer critiquing their analysis leading to this reason until Section V.

To analyze the temperature dependence, the authors first constructed their theory of electron motion. They supposed that no matter what process caused the electron to move from donor to donor, if it were phonon-activated and if it were due to impurity conduction, the corresponding transition rate U would be proportional to the number of phonons which could stimulate a transition. They then supposed that the activation energy for impurity conduction ϵ_i , where the i refers to the i^{th} impurity conduction process, was characteristic of the phonon energy Δ_{ij} . With these two assumptions, they arrived at the following expression

$$U \propto \frac{1}{\exp(\beta\epsilon_i)-1} \sim \exp(-\beta\epsilon_i) \quad . \quad (11)$$

One should note here that ϵ_j , or at least the hopping conduction ϵ_3 as shown earlier, is not characteristic of the phonon energy Δ_{ij} needed for a single hop from donor to donor. It is the sum of many phonon energies necessary to excite a carrier from its lowest state near an acceptor to a state of quasi-free conduction. Furthermore, the electron statistics which introduce an additional temperature dependence are not included in Equation (11). Thus Equation (11) does not actually correspond to the transition rate for hopping conduction.

Secondly, Gershenzon, et al., converted their line width data to frequency values which they then compared with the theoretical U . These frequency values, which here shall be called ω_N , the observed narrowing frequency, were obtained by assuming Equation (3), replacing ω_h by ω_N , solving for ω_N , and substituting experimental values for ΔH_{EXP} . Thus,

$$\omega_N = \frac{g \mu_B (\Delta H_{hfs}^2)}{\hbar (\Delta H_{EXP})} \quad . \quad (12)$$

Note that they have used the incorrect ΔH_{hfs}^2 for $\langle H^2 \rangle_{ave}$. Their ω_N vs. T curves were similar to those we have derived in Section V, Figure 12, except for the change in the scale of the ordinate due to the correct expression for $\langle H^2 \rangle_{ave}$. They then extrapolated the ω_N vs. T curves to $T = 0$ and found a $T = 0$ intercept which they attributed to temperature independent exchange narrowing. Adding this intercept to U in Equation (11), they then compared

$U' = U + \omega_N(T=0)$, their theoretical expression for the total narrowing frequency to ω_N , the observed values for the narrowing frequency. They found that the theoretical plot of U' vs. T increased considerably faster with increasing T than the experimental curves of ω_N vs. T . Apparently ω_N does not have an $\exp(-\beta\epsilon_i)$ dependence. This discrepancy was used to reject electron motion as a mechanism for explaining the observed temperature part of the line narrowing.

The other reason for rejecting electron motion was because it did not predict the expected compensation dependence in the line width. They noted that an arsenic-doped germanium sample with high compensation had the unnarrowed spectrum similar to that of a sample with low donor concentration. This sample, however, possessed an N_D comparable to that of an uncompensated sample that would exhibit narrowing (i.e., $1.2 \times 10^{16} \text{ cm}^{-3}$). Since higher compensation should intuitively increase the mobility of the electron, according to impurity conduction theory, they argued that the spectrum should have narrowed, not broadened. Combining these results with those previously discussed, they concluded that electron motion among the impurity sites was not the effective narrowing mechanism necessary to explain the temperature independent or temperature dependent observations.

However, since their theory of electron motion did not contain the proper temperature factors nor was it proper to use ϵ_i where they did, it cannot be concluded from their discussion that hopping is not involved in the temperature dependence. But it does appear from

their argument on the compensation dependence that hopping may not be the dominating narrowing mechanism and is certainly not the only one. However, no one has deduced the compensation dependence of the average hopping rate as yet, so a definite conclusion on the matter cannot be reached. Since such compensation dependence is derived in Section III of this thesis, further comparison with experiment is deferred until after such a derivation (in Section V).

The intent of this thesis should be re-emphasized at this point. Before any further meaningful conclusions can be reached concerning phonon-induced tunneling as a possible narrowing process, the correct equation for the average hopping transition rate ω_h should be found. It is evident from the discussion of Equations (4) - (6) that transitions between other than nearest neighbors must be considered and that the geometrical distributions of these neighbors must be considered. Moreover, the averaging process must take into account the distributions of electrons on donors. Finally, before any quantitative comparison with data can be done, the correct expression for $\langle H^2 \rangle_{ave}$ must be found. Then theory and experiment can be compared, and more meaningful conclusions can be determined.

III. CALCULATION OF THE AVERAGE HOPPING TRANSITION RATE

A. THE MODEL AND THE METHOD

The major portion of this thesis deals with the calculation of an average hopping transition rate ω_h , characteristic of the electron ensemble. Before performing that calculation, the ensemble must first be described, ω_h must be defined, and methods used in the averaging process must be explained.

Due to the success of the Miller and Abrahams^{17b} theory of impurity conduction, an effort will always be made to stay as close as possible to the model of phonon-induced tunneling used in that theory. Thus, the crystal is a group IV semiconductor with dielectric constant k_0 and doped with N_D donors and N_A acceptors randomly distributed. The compensation ratio $K = N_A/N_D$ is less than unity, implying that $N_D - N_A$ donors are occupied and N_A are vacant. Because of the negative charge of the nearest acceptors, the ground states of the donors are perturbed. If the unperturbed ground state is taken as $E=0$, then the ground state energy of the i^{th} donor is obtained from Equations A-6 as

$$E_i = \langle \psi_i | V_a | \psi_i \rangle \approx \frac{e^2}{k_0 r_{iA}} \quad , \quad (13)$$

where r_{iA} is the distance from donor i to the nearest acceptor.

The definition of the average transition rate over this ensemble must be in agreement with the concepts of motional narrowing. Since the $2I+1$ line spectrum in Figure 1(a) is typical

of donor electrons in the donor ground state⁴ and since this is the spectrum presumed to be narrowed by motion, only electrons in the donor ground state are considered. In addition, the transitions of interest which are considered to contribute to motional narrowing are those from one ground state directly to another ground state. Effects of intermediate transitions through the excited states are assumed to be small at low temperatures since they require a relatively large phonon energy.

Combining these ideas, ω_h can be formally defined as the total number of direct hops between ground states per unit time per electron in the donor ground state. If U_{ij} is the transition rate of an electron from the ground state on a specific donor i to the ground state on a donor j , then ω_h is the summation of U_{ij} over all pairs of occupied ground state donors and unoccupied donors, divided by the number of electrons in the ground state. That is,

$$\omega_h = \frac{\sum_{\substack{i(\text{ground state} \\ \text{occupied})}} \sum_{j(\text{vacant})} U_{ij}}{\sum_{\substack{i(\text{ground state} \\ \text{occupied})}} 1} . \quad (14)$$

As stated earlier, Miller and Abrahams^{17b} have calculated U_{ij} and a brief rederivation is given in Appendix A. For convenience the results are restated here as

$$U_{ij} = \frac{1}{B} r_{ij}^{3/2} \exp(-2r_{ij}/a) \frac{\Delta_{ij}}{[1-\exp(-\beta\Delta_{ij})]} , \quad (15)$$

where

$$\frac{1}{B} = \left(\frac{E_1^2}{\pi \rho_{oc} 5 \hbar^4} \right) \left(\frac{2e^2}{3k_o a^2} \right)^2 \left(\frac{1}{n} \right) \left\{ \frac{\pi a}{4 \left(\frac{a^2}{b^2} - 1 \right)} \right\}^{\frac{1}{2}} .$$

The values of the constants in $1/B$ are enumerated in Appendix A; r_{ij} is the distance between the two sites and a is the transverse Bohr radius of a single valley wave function; $\Delta_{ij} = E_i - E_j$ is the energy difference between the ground states of i and j .

The first step in reducing ω_h to a form which can more easily be interpreted is to take the electron ensemble into account mathematically. If a function f_i^α is defined as the probability that the α state on i is occupied by an electron, then Equation (14) can be rewritten as

$$\omega_h = \frac{\sum_{i=1}^{N_D} \sum_{j=1}^{N_D} f_i^0 (1 - \sum_{\delta} f_j^\delta) U_{ij}}{\sum_{i=1}^{N_D} f_i^0} , \quad (16)$$

where f_i^0 assures that the ground state on i is occupied and $(1 - \sum_{\delta} f_j^\delta)$ makes certain that donor j is completely vacant. Equation (16) now contains the statistics of the electrons distribution, which have been left out of all previous treatments of the narrowing problem. (Note, however, that these statistics were not left out of Miller and Abrahams' calculation of the contribution of hopping to the resistivity. Equation (16) is in many ways similar to

Equation III-2 in Reference 17b.¹⁹⁾ In Part B of this section the f_i^α distribution functions are discussed in greater detail and shown to have strong temperature and compensation dependences. Thus, their inclusion in the calculation will significantly alter the final form of ω_h from the previously used expression of $U_{ij}(R_D, \Delta)$ (see Part II).

The second method for simplifying ω_h involves a mathematical treatment of the impurity ensemble to perform the i and j summations over all donors. Since the impurities are randomly distributed and since they number so many, the range of values which a microscopic parameter, such as r_{ij} , Δ_{ij} , or E_i , may take on is nearly continuous. The summations over i and j can thus be changed to integrals over the parameters of which $\omega_{ij} = [(1 - \sum_{\delta} f_j^\delta) U_{ij}]$ and f_i^0 are a function, if the integrands are weighted by the probability distributions of these parameters. This concept can be expressed abstractly as follows

$$\omega_h = \frac{\sum_{i=1}^{N_D} \sum_{j=1}^{N_D} f_i^0 \omega_{ij}(\lambda_1, \lambda_2, \lambda_3, \dots)}{\sum_{i=1}^{N_D} f_i^0(\lambda_1, \lambda_2, \lambda_3, \dots)}$$

$$\Rightarrow \frac{\int d\lambda_1 d\lambda_2 d\lambda_3 \dots F(\lambda_1)F(\lambda_2)F(\lambda_3) \dots f_i^0 \omega_{ij}(\lambda_1, \lambda_2, \lambda_3, \dots)}{\int d\lambda_1 d\lambda_2 d\lambda_3 \dots F(\lambda_1)F(\lambda_2)F(\lambda_3) \dots f_i^0(\lambda_1, \lambda_2, \lambda_3, \dots)}, \quad (17)$$

where the F functions represent the probability distributions of the λ parameters. The actual parameters are, as will be shown, r_{in} , Δ_{in} , and E_i . Part C of this section is concerned with the means of changing the summations into integrations and with finding valid probably distributions for r_{in} , Δ_{in} , and E_i .

At each stage of this derivation it is useful to state the current form for ω_h . The result of the present section is

$$\omega_h = \frac{\sum_{i=1}^{N_D} \sum_{j=1}^{N_D} f_i^0 (1 - \sum_{\delta} f_j^{\delta}) \frac{1}{B} r_{ij}^{3/2} \exp(-2r_{ij}/a) \frac{\Delta_{ij}}{[1 - \exp(-\beta\Delta_{ij})]}}{\sum_{i=1}^{N_D} f_i^0} \quad (18)$$

B. THE ELECTRON STATISTICS

1. Application of the Electron Distribution

The distribution of electrons and vacancies on donors is embodied in the f_i^{α} . By considering the detailed balance, Miller^{17c} has already evaluated this function as

$$f_i^{\alpha} = \frac{\exp(-\beta(E_i^{\alpha} - \zeta))}{1 + \sum_{\delta} \exp(-\beta(E_i^{\delta} - \zeta))} \quad (19)$$

where E_i^{α} is the energy of the electron in the α state on donor i . Equation (19) can also be written as the product of a Maxwell-Boltzman distribution of the excited states and a simple Fermi distribution of the ground state energies or

$$f_i^\alpha = \left[\frac{\exp(-\beta\Delta_e^\alpha)}{\sum_{\delta} \exp(-\beta\Delta_e^\delta)} \right] \frac{1}{[1+\exp \beta(E_i-\zeta_g)]} , \quad (20)$$

where $\Delta_e^\alpha = E_i^\alpha - E_i$ is the difference in the energy of the α^{th} excited state from the ground state energy. The first factor in Equation (20) corresponds to the occupation probability of a particular state α on donor i , while the second corresponds to the probability that donor i is occupied.

The symbol ζ stands for the Fermi energy for the entire electron ensemble, while ζ_g is the Fermi energy if the ground states only were considered. The two are related by^{17b,c}

$$\exp(\beta\zeta_g) = \exp(\beta\zeta) \sum_{\delta} \exp(-\beta\Delta_e^\delta) . \quad (21)$$

Noting that the total number of electrons on the donors is $N_D - N_A$, one may determine ζ_g by solving the following equation

$$\sum_{i,\alpha} f_i^\alpha = N_D - N_A \quad (22)$$

or

$$\sum_{i=1}^{N_D} \frac{1}{1+\exp(\beta(E_i-\zeta_g))} = N_D - N_A . \quad (23)$$

Consequently, ζ may then be obtained from Equation (21).

From Equations (20) and (23) it can easily be shown that the three quantities f_i^0 , $(1-\sum_{\delta} f_j^\delta)$, and $\sum_i f_i^0$ needed to evaluate ω_h in

Equation (18) are

$$f_i^0 = \frac{1}{Z(T)} \frac{1}{1 + \exp(\beta(E_i - \zeta_g))} , \quad (24a)$$

$$(1 - \sum_{\delta} f_j^{\delta}) = \frac{1}{1 + \exp(-\beta(E_j - \zeta_g))} = \frac{1}{1 + \exp(-\beta(E_i - \Delta_{ij} - \zeta_g))} , \quad (24b)$$

and

$$\sum_i f_i^0 = \frac{1}{Z(T)} \sum_i \frac{1}{1 + \exp(\beta(E_i - \zeta_g))} = \frac{N_D - N_A}{Z(T)} , \quad (24c)$$

where $Z(T) = \sum_{\delta} \exp(-\beta \Delta_e^{\delta})$ is the partition function for the levels on a single donor atom. The expression for ω_h then becomes

$$\begin{aligned} \omega_h = & \frac{1}{(N_D - N_A)} \sum_{i=1}^{N_D} \sum_{j=1}^{N_D} \left[\frac{1}{1 + \exp(\beta(E_i - \zeta_g))} \right] \left[\frac{1}{1 + \exp(-\beta(E_i - \Delta_{ij} - \zeta_g))} \right] \\ & \times \frac{1}{B} r_{ij}^{3/2} \exp(-2r_{ij}/a) \frac{\Delta_{ij}}{[1 - \exp(-\beta \Delta_{ij})]} . \end{aligned} \quad (25)$$

2. Calculation of the Fermi Energy

Because the ground state Fermi energy in Equation (25) is unknown at the present time, it is necessary to evaluate ζ_g as a function of the three important sample parameters N_D , N_A (or K), and T . The calculation is almost identical to that done by Miller and Abrahams.^{17b} Rewriting Equation (23) and considering the E_i to be close together, one obtains

$$K = \frac{N_A}{N_D} = \frac{1}{N_D} \sum_{i=1}^{N_D} \frac{1}{1 + \exp(-\beta(E_i - \zeta_g))} = \int_0^{\infty} \frac{F(E) dE}{1 + \exp(-\beta(E - \zeta_g))} , \quad (26)$$

where

$$F(E) = (3E_A^3/E^4) \exp(-(E_A/E)^3) ,$$

$$E_A = e^2/k_0 R_A ,$$

and

$$R_A = (3/4\pi N_A)^{1/3} .$$

The density of states, $F(E)$, is obtained by assuming a Poisson distribution of nearest neighbor acceptors. It is discussed in detail in Part C of this section. Equation (26) may be evaluated analytically, using certain approximations which will be useful later in the evaluation of ω_h . It may also be evaluated numerically using a relatively simple computer program.

In the analytical calculation, two regions of interest afford conditions which allow Equation (26) to be approximated. The first is the low temperature region, the one used by Miller and Abrahams. Integrating Equation (26) once by parts, they obtained

$$(1-K) = \beta \int_{-\beta\zeta_g}^{\infty} \frac{\exp(-(E_A/E)^3) dE}{[1 + \exp(\beta(E - \zeta_g))][1 + \exp(-\beta(E - \zeta_g))]} . \quad (27)$$

Since for low temperatures the denominator is peaked at $E = \zeta_g$, removal of the numerator from under the integral, evaluating it at $E = \zeta_g$, and integration of the denominator yields

$$(1-K) = \frac{\exp(-(E_A/\zeta_g)^3)}{1+\exp(-\beta\zeta_g)} \quad . \quad (28)$$

In order to use this method the $\exp(-(E_A/E)^3)$ function must be slowly varying in the region of E spanned by the product of the electron distribution functions in Equation (27), which is peaked at $E=\zeta_g$. Mathematically, this means the following inequality must be valid

$$\left. \frac{d}{dE} \left[\frac{\exp(-(E_A/E)^3)}{\exp(-(E_A/E)^3)} \right] \right|_{\zeta_g} 3.52 k_B T \ll 1 \quad , \quad (29a)$$

since the width at half-maximum of the denominator in energy is $3.52k_B T$. Evaluating Inequality (29a) and substituting the appropriate ζ_g , Equation (30) below, one can obtain a statement of what the phrase "low T " means,

$$T \ll \frac{E_A}{10.6 k_B [-\ln(1-K)]^{4/3}} \equiv T_C \quad . \quad (29b)$$

For a typical acceptor concentration of 10^{14} cm^{-3} , T_C is about 340°K for $N_D = 10^{16} \text{ cm}^{-3}$ in Ge and about $1.06 \times 10^4 \text{ }^\circ\text{K}$ for $N_D = 10^{17} \text{ cm}^{-3}$ in Si. The experiments at liquid helium temperatures are well below these temperatures.

Finally, solving Equation (28) for positive ζ_g and considering $\exp(-\beta\zeta_g)$ small, one obtains for this low T approximation

$$\zeta_g = \frac{E_A}{[-\ln(1-K)]^{1/3}} \quad , \quad (30)$$

which is the Fermi energy one would obtain if he evaluated equation (26) at $T=0$. Note that as long as Inequality (29b) is satisfied, $\beta\zeta_g \gg 0$ is also satisfied. Thus the dropping of the $\exp(-\beta\zeta_g)$ term in the denominator in Equation (28) is a good approximation for low T. Equation (30) should be consistent with the fact that as the compensation becomes closer to unity, the $f_i^\alpha(T=0)$ should show that fewer donors with energies from 0 to ζ_g are occupied. Substitution of Equation (30) into Equation (20) shows that this is indeed the case. Finally, if the compensation remains fairly small, the Fermi energy can be approximated using Equation (30) as

$$\zeta_g = E_D \quad , \quad (31)$$

which is the value quoted previously in Equation (10).

The second region of interest in which Equation (26) may be approximately solved for ζ_g is a high temperature region. Here an inequality similar to Inequality (29a) must be satisfied, namely,

$$\left. \frac{d}{dE} \ln[1+\exp(-\beta(E-\zeta_g))] \right|_{E_0} (0.66 E_A) \ll 1 . \quad (32a)$$

This guarantees that the distribution of the holes given by Equation (26) must be slowly varying in the energy region near the peak of $F(E)$, which is peaked at a value

$$E_0 = (3/4)^{1/3} E_A = \frac{e^2}{k_0} (\pi N_A)^{1/3} .$$

Note that the width of the density of states at half-maximum is $0.66 E_A$. Evaluating Inequality (32a) and using the high T value for ζ_g , Equation (34), one obtains the high T condition

$$T \gg \frac{0.66 E_A}{k_B} (1-K) \equiv T'_C . \quad (32b)$$

For the typical N_A of 10^{14} cm^{-3} chosen earlier, $T'_C = 5.1^\circ\text{K}$ for Ge and $T'_C = 7.3^\circ\text{K}$ for Si. Hence, for the high T approximation to hold, the temperature must be much higher than liquid helium temperatures, according to Inequality (32b).

To proceed with the high T approximation, the $[1+\exp(-\beta(E-\zeta_g))]$ function can be removed from the integral in Equation (26) and evaluated at E_0 . One then obtains

$$K = \frac{1}{1 + \exp(-\beta(E_0 - \zeta_g))} \int_0^{\infty} F(E) dE = \frac{1}{1 + \exp(-\beta(E_0 - \zeta_g))} . \quad (33)$$

Thus,

$$\zeta_g = E_0 + k_B T \ln\left(\frac{1-K}{K}\right) . \quad (34)$$

Substitution of Equation (34) into Equation (24a) or (24b) and evaluating at $E_i = E_0$ shows the significance of the high T approximation. For higher temperatures the probability that a donor is occupied is simply $(1-K)$ and the probability that one is vacant is about K .

Finally, Equation (26) can be solved numerically for ζ_g . The details of the method are presented in Appendix C. Figures 5, 6, and 7 plot the exact solutions for ζ_g for hypothetical samples of n-type germanium. Figure 5 shows how ζ_g varies with donor concentration at various temperatures if each sample with a different N_D is assumed to have the same acceptor concentration $N_A = 5.0 \times 10^{13} \text{ cm}^{-3}$. Figure 6 shows the dependence of ζ_g on temperature for various N_D ; again all the samples are assumed to have $N = 5.0 \times 10^{13} \text{ cm}^{-3}$. The $T=0$ intercepts of the curves give the low T approximations. Note how this approximation fails for $T > 4 \text{ }^\circ\text{K}$. The high T approximation (Equation (34)) for all these curves is also shown. Note that it is still not a very good approximation for $T = 12 \text{ }^\circ\text{K}$. Lastly, Figure 7 shows the dependence of ζ_g on compensation for a sample with $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$ for various temperatures. Note that $\zeta_g \rightarrow -\infty$

Figure 5. The Fermi energy of the ground states vs. the donor concentration in n-type germanium calculated by a computer from Equation (26). A constant N_A of $5.0 \times 10^{13} \text{ cm}^{-3}$ was chosen. The curves shown correspond to: (a) $T = 2 \text{ }^\circ\text{K}$, (b) $T = 6 \text{ }^\circ\text{K}$, and (c) $T = 10 \text{ }^\circ\text{K}$. All curves for $T > 0$ go to $\zeta_g = -\infty$ at $N_D = N_A$, as they should. If $T=0$, $\zeta_g = 0$ for $N_D = N_A$.

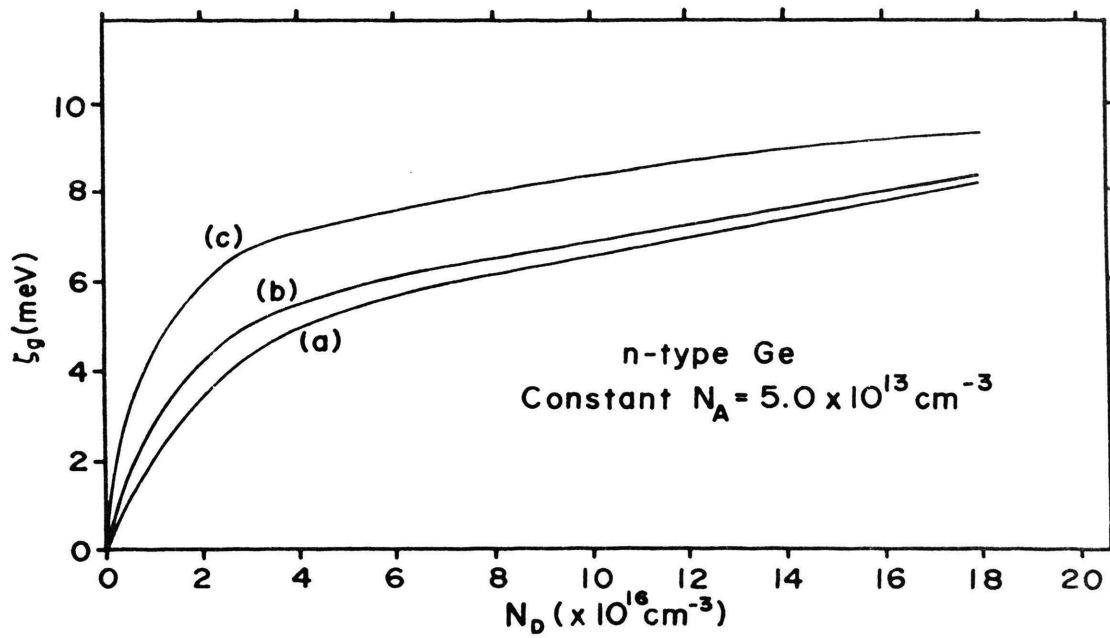


Figure 5

Figure 6. The Fermi energy of the ground states vs. temperature for various donor concentrations in n-Ge as calculated by computer from Equation (26). A constant N_A of $5.0 \times 10^{13} \text{ cm}^{-3}$ was chosen for all hypothetical samples. The curves correspond to: (a) $N_D = 3.4 \times 10^{16} \text{ cm}^{-3}$, (b) $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$, (c) $N_D = 7.0 \times 10^{16} \text{ cm}^{-3}$, and (d) $N_D = 1.8 \times 10^{17} \text{ cm}^{-3}$. The $T=0$ intercepts are given by Equation (30), the low T approximation. Also illustrated is the high T approximation (dashed curve) valid for curves (a) through (d).

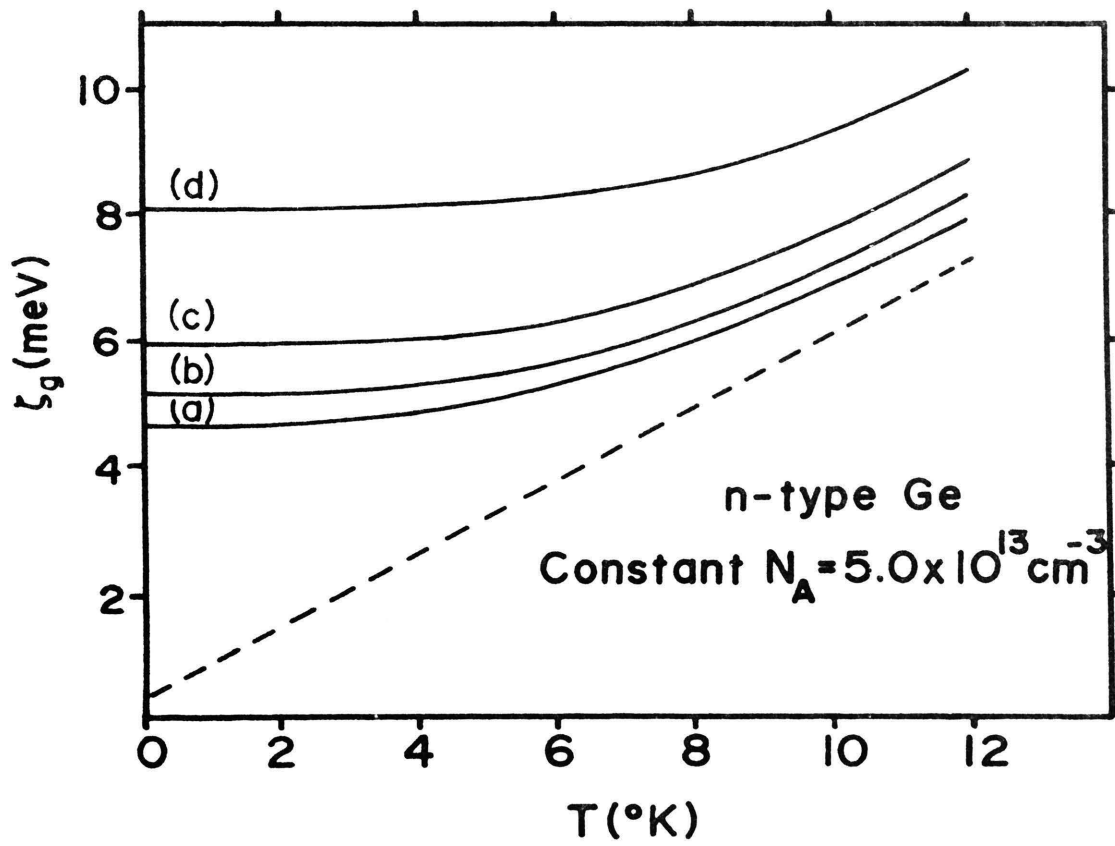


Figure 6

Figure 7. The Fermi energy of the ground states vs. compensation for various temperatures in n-Ge as calculated by computer from Equation (26). A constant $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$ was chosen. The curves correspond to: (a) $T=0^\circ\text{K}$ (also low T approximation, given by Equation (30)), (b) $T=8^\circ\text{K}$, and (c) $T=16^\circ\text{K}$. Also illustrated is the high T approximation from Equation (34) (dashed curve) for 16°K . Note that it becomes a better approximation for curve (c) at high K and low K.

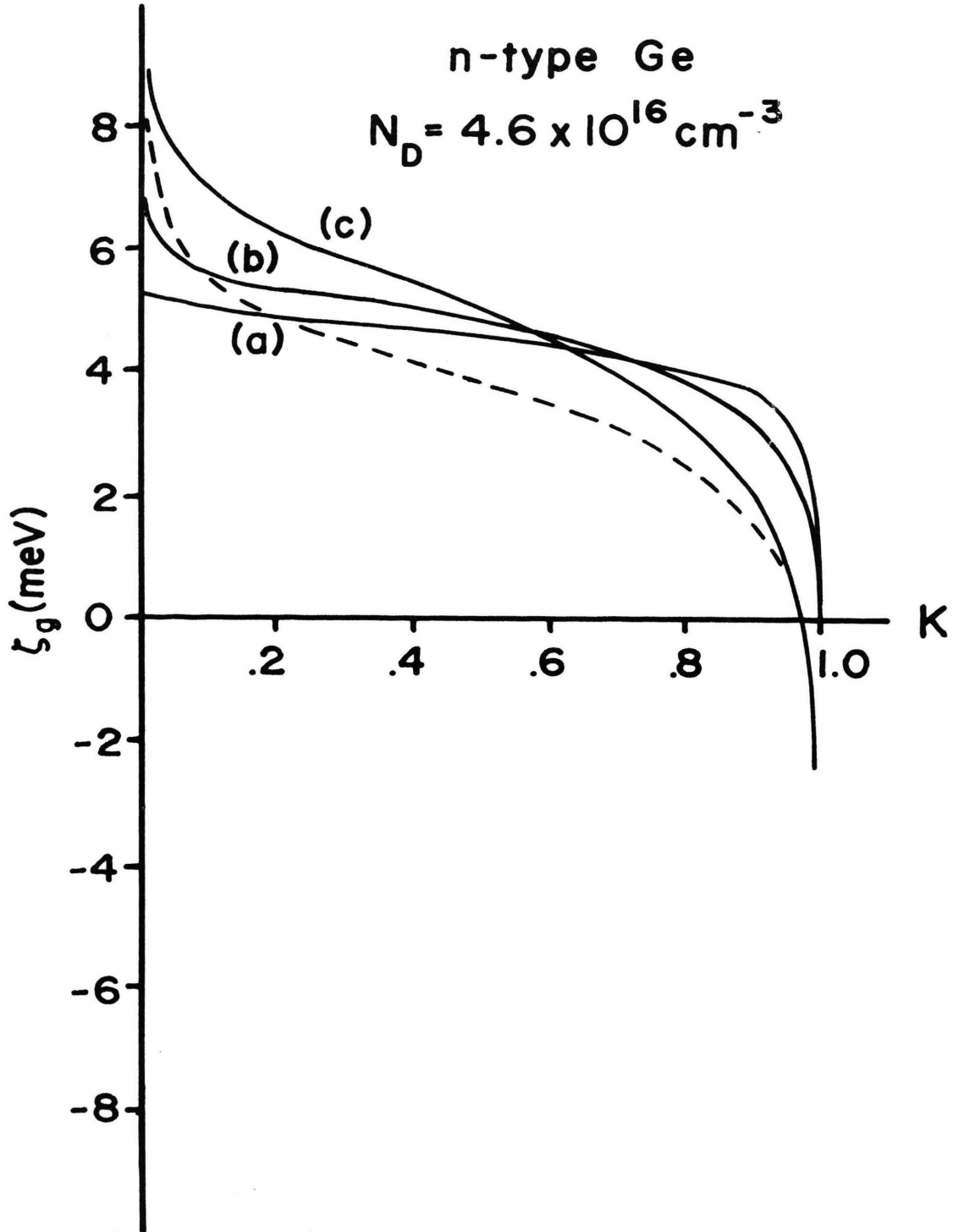


Figure 7

as $K \rightarrow 1$ if $T > 0$. Also note how the high T approximation only begins to approximate ζ_g even at $T = 16$ °K.

C. THE DISTRIBUTION OF THE IMPURITIES

The summations in Equation (25) may be converted to more easily handled integrals. To gain physical insight into these methods, it is very useful to break the ensemble average into two operations. First a quantity ω_i is defined as

$$\omega_i = \sum_{j=1}^{N_D} (1 - \sum_{\delta} f_j^{\delta}) U_{ij} = \sum_{j=1}^{N_D} \omega_{ij} \quad (35a)$$

The j index in this summation enters ω_{ij} through the spacial parameter r_{ij} and the phonon energy parameter Δ_{ij} [see Equation (25)]. Thus, it is possible to evaluate ω_i by integrating over the distributions of these two parameters. To calculate ω_h , ω_i must be averaged over the sites whose ground states are occupied. Hence,

$$\omega_h = \frac{\sum_{i=1}^{N_D} f_i^0 \omega_i}{\sum_{i=1}^{N_D} f_i^0} \quad (35b)$$

The i index enters the functions $f_i^0 \omega_i$ and f_i^0 through the parameter E_i . Therefore these summations can be performed by integrations over the distribution function of the E_i 's, commonly called the density of states function.

This procedure has an interesting physical interpretation. If one thinks of ω_i as the total transition probability per unit time

from donor i , then the right side of Equation (35a) corresponds to a summation of the transition probability U_{ij} over final states (over all possible vacant donors) and the right side of Equation (35b) corresponds to averaging over the initial states.

1. The First Summation--The Spacial and Phonon Energy Distributions

If the j sum is performed first, then for the moment only a single donor i is being considered. The j index can then be thought of as the neighbor number n , which denotes the ordinal proximity of a certain neighboring donor. For a specific donor i , the distance to the n^{th} nearest neighbor r_{in} and the ground state energy difference Δ_{in} will vary. However, since $\omega_{in}(r_{in}, \Delta_{in})$ will be summed over all i , only an average $\overline{\omega_{in}}$ over all possible r_{in} and Δ_{in} in the random distribution of donors is needed.

To average over all possible r_{in} and Δ_{in} , one needs the probability, $f_n(r_{in})$, that the n^{th} nearest neighbor is at a distance r_{in} . For a random Poisson distribution of particles with average concentration $N_D = (3/4\pi R_D^3)$, the probability that the n^{th} nearest donor to the donor i is in a spherical shell with radius r_{in} and width dr_{in} , centered about donor i , is^{17b}

$$f_n(r_{in}) = \frac{3 r_{in}^{3n-1} \exp(-(r_{in}/R_D)^3)}{R_D^{3n} (n-1)!} . \quad (36)$$

Two forms for Equation (36) have already been used in Equations (8a) and (9). The nearest neighbor form, $n=1$, will also be needed for calculation of the density of states later on.

Since ω_{in} is a function of Δ_{in} , a distribution for this parameter must also be derived. In general, since Δ_{in} will vary over the aforementioned spherical shell of radius r_{in} , this distribution will be a function of both the orientation and magnitude of r_{in} . It will also be a function of E_i . The method used to calculate such a distribution is to consider the donor n (at a particular point on the shell of radius r_{in}), the donor i , and the nearest acceptor to form a triangle. Then, one fixes the distance from i to the acceptor $r_{iA} = e^2/k_0 E_i$ and fixes the separation r_{in} . This fixing of the two sides of the triangle assures that Δ_{in} is a function of only the angle between these sides, denoted by θ .

One may calculate the normalized probability distribution for Δ_{in} , $G(\Delta_{in})$, by first finding a normalized distribution $g(\theta)$ and then changing variables to the phonon energy parameter through an appropriate relation between θ and Δ_{in} . This change in variables is performed by a common mathematical technique

$$G(\Delta_{in}) = \left| g(\theta) \frac{d\theta}{d\Delta_{in}} \right| . \quad (37)$$

The absolute value sign is used since all probability distributions are positive functions. The function $g(\theta)$ may be derived by noting that in a random distribution of donors, the n^{th} donor can be in any element of solid angle on the r_{in} sphere. The probability of the n^{th} donor being in $d\Omega$ is then

$$\frac{d\Omega}{4\pi} = \frac{\sin\theta \, d\theta}{4\pi} \, d\phi \quad \begin{array}{l} 0 < \theta < \pi \\ 0 < \phi < 2\pi \end{array} \quad (38)$$

and zero elsewhere, where ϕ is the azimuthal angle about r_{iA} . Since Δ_{in} is not a function of ϕ , the right side of Equation (38) may be integrated over ϕ . The probability that r_{in} makes an angle between θ and $\theta+d\theta$ then becomes

$$\begin{aligned} g(\theta) &= \frac{\sin \theta}{2} & 0 < \theta < \pi \\ &= 0 & \text{elsewhere} \end{aligned} \quad (39)$$

Combining Equations (37) and (39), one obtains

$$\begin{aligned} G(\Delta_{in}) &= \frac{1}{2} \left| \frac{d(\cos \theta)}{d\Delta_{in}} \right| & 0 < \theta < \pi \\ &= 0 & \text{elsewhere} \end{aligned} \quad (40)$$

The final step to perform before one can calculate $G(\Delta_{in})$ is to determine the relation between θ and Δ_{in} . This is done by using the law of cosines with the expression

$$\begin{aligned} \Delta_{in} &= E_i - E_n \\ &= \frac{e^2}{k_o} \left[\frac{1}{r_{iA}} - \frac{1}{\sqrt{r_{iA}^2 + r_{in}^2 - 2r_{iA}r_{in}\cos\theta}} \right] \end{aligned} \quad (41)$$

Equation (41) yields

$$\cos\theta = \frac{1}{2} \left[\frac{e^2}{k_o E_i r_{in}} + \frac{k_o E_i r_{in}}{e^2} - \frac{e^2}{k_o E_i r_{in}} \frac{1}{\left(1 - \frac{\Delta_{in}}{E_i}\right)^2} \right] \quad (42)$$

Thus, using Equations (40) and (42) one finds that

$$G(\Delta_{in}) = \frac{e^2}{2k_0 E_i^2 r_{in}} \frac{1}{\left(1 - \frac{\Delta_{in}}{E_i}\right)^3} \quad \Delta^- < \Delta_{in} < \Delta^+ \quad (43)$$

$$= 0 \quad \text{elsewhere} \quad .$$

By inserting the limits of $\theta=0$ and $\theta=\pi$ into Equation (41), the limits on $G(\Delta_{in})$ can be found. If $0 < r_{in} < r_{iA} = e^2/k_0 E_i$, then

$$\Delta^- = \frac{-E_i r_{in}}{\left(\frac{e^2}{k_0 E_i} - r_{in}\right)}$$

and

$$\Delta^+ = \frac{E_i r_{in}}{\left(\frac{e^2}{k_0 E_i} + r_{in}\right)} \quad . \quad (44)$$

If $e^2/k_0 E_i < r_{in} < \infty$, then

$$\Delta^- = \frac{-E_i \left(\frac{2e^2}{k_0 E_i} - r_{in}\right)}{\left(r_{in} - \frac{e^2}{k_0 E_i}\right)}$$

and

$$\Delta^+ = \frac{E_i r_{in}}{\left(\frac{e^2}{k_0 E_i} + r_{in}\right)} \quad . \quad (45)$$

Equations (36) and (43) now give normalized distributions which allow the calculation of $\overline{\omega_{in}}$. Since $G(\Delta_{in})$, Δ^- , and Δ^+ are functions

of r_{in} , the Δ_{in} integral must occur inside the r_{in} integral. Thus

$$\overline{\omega_{in}} = \int_0^{\infty} dr_{in} \int_{\Delta^-}^{\Delta^+} d\Delta_{in} f_n(r_{in}) G(\Delta_{in}, r_{in}) \omega_{in}(\Delta_{in}, r_{in}, E_i) \quad (46)$$

Noting that $\sum_n \overline{\omega_{in}}$ may be substituted for $\sum_j \omega_{ij}$ and inserting Equation (46) into Equation (35) one obtains for ω_h

$$\omega_h = \frac{1}{(N_D - N_A)B} \sum_i \frac{1}{1 + \exp(\beta(E_i - \zeta_g))} \sum_n \int_0^{\infty} dr_{in} \int_{\Delta^-}^{\Delta^+} d\Delta_{in} G(\Delta_{in}) f_n(r_{in}) \frac{1}{1 + \exp(-\beta(E_i - \zeta_g - \Delta_{in}))} r_{in}^{3/2} \exp(-2r_{in}/a) \frac{\Delta_{in}}{[1 - \exp(-\beta\Delta_{in})]} \quad (47)$$

2. The Second Summation--The Density of States

The sum over all i donors may be performed by summing over all energies E_i . This approach then allows a change from the summation over i to an integration over a density of states, provided that the energy states are close together. The appropriate density of states is found by using Equation (13) to relate r_{iA} to an energy E_i . The probability that the nearest acceptor is in a spherical shell of radius r_{iA} about i can be obtained by setting $n=1$ in Equation (36) and using R_A for acceptors instead of R_D .^{17b} Thus,

$$f(r_{iA}) = \frac{3r_{iA}^2}{R_A^3} \exp(-(r_{iA}/R_A)^3) \quad (48)$$

The variable change to E_i is performed using a relation similar to Equation (37). Hence,

$$F(E_i) = \left| f(r_{iA}) \frac{dr_{iA}}{dE_i} \right| = \frac{3E_A^3}{E_i^4} \exp(-(E_A/E_i)^3) \quad . \quad (49)$$

To sum over all i , one simply multiplies by N_D and integrates the normalized $F(E)$ over the appropriate function. (Note that this is the same method used in Part B to sum the distribution over all the donors to find the ground state Fermi energy.)

D. THE FORMAL EXPRESSION FOR THE AVERAGE HOPPING TRANSITION RATE

The final step in deriving an integral expression for ω_h involves performing the summation over neighbor numbers n . Since the subscripts on the integration variables in Equation (46) may be dropped, and since the limits on these integrals do not vary with n , the sole function which remains under the \sum_n sign is $f_n(r)$. Note however that

$$\begin{aligned} \sum_{n=1}^{\infty} f_n(r) &= \frac{3r^2}{R_D^3} \exp[-(r/R_D)^3] \sum_{n=1}^{\infty} \frac{r^{3(n-1)}}{R_D^{3(n-1)} (n-1)!} \\ &= \frac{3r^2}{R_D^3} = 4\pi N_D r^2 \quad . \end{aligned} \quad (50)$$

Using Equation (47) for ω_h , Equation (49) to change the sum over i to an integral over $F(E)dE$, and Equation (50) to perform the sum over neighbor numbers, one obtains the final expression for the average transition rate

$$\begin{aligned}
\omega_h = & \frac{1}{B(1-K)} \int_0^\infty dE \frac{3E_A^3}{E^4} \exp[-(E_A/E)^3] \\
& \left\{ \int_0^{e^2/k_0 E} dr 4\pi N_D r^2 \int_{-Er/(e^2/k_0 E-r)}^{Er/(e^2/k_0 E+r)} d\Delta \frac{e^2}{2k_0 E^2 r} \frac{1}{(1-\frac{\Delta}{E})^3} \right. \\
& \times \left[\frac{1}{1+\exp(\beta(E-\zeta_g))} \right] \left[\frac{1}{1+\exp(-\beta(E-\Delta-\zeta_g))} \right] r^{3/2} \exp(-2r/a) \\
& \times \frac{\Delta}{1-\exp(-\beta\Delta)} \\
& + \int_{e^2/k_0 E}^\infty dr 4\pi N_D r^2 \int_{\frac{-E(2e^2/k_0 E-r)}{(r-e^2/k_0 E)}}^{Er/(e^2/k_0 E+r)} d\Delta \frac{e^2}{2k_0 E^2 r} \frac{1}{(1-\frac{\Delta}{E})^3} \\
& \times \left[\frac{1}{1+\exp(\beta(E-\zeta_g))} \right] \left[\frac{1}{1+\exp(-\beta(E-\Delta-\zeta_g))} \right] r^{3/2} \exp(-2r/a) \\
& \left. \times \frac{\Delta}{1-\exp(-\beta\Delta)} \right\} . \tag{51}
\end{aligned}$$

Equation (51) represents the complete expression for the average transition rate one obtains by using the Miller and Abrahams model and their calculational techniques over the electron and impurity ensembles. It is still not in a very desirable form and it appears

that the expression cannot be reduced further without approximating it or numerically performing the integrations.

However, before examining ω_h under certain approximations, a few points concerning the N_D , K (or N_A) and T dependences should be made. The N_D dependence is in the multiplicative factor of N_D in the second integral and an indirect dependence which occurs through ζ_g . The K dependence of ω_h is in the $1/(1-K)$ function, the Fermi energy ζ_g , the density of states, and the energy distribution $G(\Delta)$.

The temperature dependence of ω_h is determined solely by the function

$$h(E, \Delta, T) = \Delta \{ [1 + \exp(\beta(E - \zeta_g))] [1 + \exp(-\beta(E - \zeta_g - \Delta))] [1 - \exp(-\beta\Delta)] \}^{-1} \quad (52)$$

as inspection of Equation (51) shows. Of the three terms in square brackets, the first is the occupied donor distribution function, the second is the unoccupied donor distribution function, and the third is a term from the phonon distribution function. Furthermore, it is now possible to mathematically prove that $\omega_h \rightarrow 0$ in the $T=0$ limit as was intuitively developed in Section II. To do this, ω_h will be found from $h(E, \Delta, T)$. Now $h(E, \Delta, T)$ can be calculated from the values of the above three mentioned terms. To evaluate these terms, it is convenient to classify the possible range of values that E , Δ , and $(E-\Delta)$ can assume. These range of values can clearly be expressed as:

$$\text{for } E, \quad [E > \zeta_g] \quad \text{or} \quad [E < \zeta_g] \quad ; \quad (53a)$$

$$\text{for } \Delta, \quad [\Delta > 0] \quad \text{or} \quad [\Delta < 0] \quad ; \quad (53b)$$

$$\text{and for } (E-\Delta), \quad [(E-\Delta) > \zeta_g] \quad \text{or} \quad [(E-\Delta) < \zeta_g] \quad . \quad (53c)$$

Then, the resulting expressions for $h(E,\Delta,T)$ in the $T=0$ limit are given below.

Case 1 ($E > \zeta_g$):

if $\Delta > 0$ and $(E-\Delta) > \zeta_g$, then

$$h \sim \Delta \exp[-\beta(E-\zeta_g)] \quad ; \quad (54a)$$

if $\Delta > 0$ and $(E-\Delta) < \zeta_g$, then

$$h \sim \Delta \exp(-\beta\Delta) \quad ; \quad (54b)$$

and if $\Delta < 0$ and $(E-\Delta) > \zeta_g$, then

$$h \sim -\Delta \exp[-\beta(E-\zeta_g)-\beta|\Delta|] \quad . \quad (54c)$$

(Note that $\Delta < 0$ and $(E-\Delta) < \zeta_g$ are not compatible with $E > \zeta_g$ and this combination has been omitted from Case 1.)

Case 2 ($E < \zeta_g$):

if $\Delta > 0$ and $(E-\Delta) < \zeta_g$, then

$$h \sim \Delta \exp[-\beta(\zeta_g-E)-\beta\Delta] \quad ; \quad (55a)$$

if $\Delta < 0$ and $(E-\Delta) > \zeta_g$, then

$$h \sim -\Delta \exp(-\beta|\Delta|) \quad ; \quad (55b)$$

and if $\Delta < 0$ and $(E-\Delta) < \zeta_g$, then

$$h \sim -\Delta \exp[-\beta(\zeta_g-E)] \quad . \quad (55c)$$

(Note that $\Delta > 0$ and $(E-\Delta) > \zeta_g$ are not compatible with $E < \zeta_g$ and this combination has been omitted from Case 2.)

Examining Equations (54) and (55) one sees that for any combination of E , Δ , and $(E-\Delta)$, $h(E,\Delta,T)$ is an exponential function of a negative number divided by $k_B T$ at low temperatures. Thus, $h(E,\Delta,T)$ goes to zero for all E and Δ as T approaches zero. Since the integral of a function whose values are all zero is zero, Equation (51) shows that

$$\omega_h \rightarrow 0 \quad \text{as} \quad T \rightarrow 0 \quad . \quad (56)$$

E. THE LOW COMPENSATION APPROXIMATION FOR THE AVERAGE HOPPING TRANSITION RATE

1. The Low K Approximation Valid for all Temperature

The integrals in Equation (51) are relatively complicated and do not appear to yield a closed form solution. Thus, either a numerical solution may be attempted or analytic approximations of the integral in certain regions of interest may be obtained. The complete numerical solution has the advantage of giving an exact answer for ω_h . However, the amount of computer time involved in performing a triple integral to find each value for ω_h is great. Approximations to the integral, on the other hand, might not yield as accurate an answer as the numerical solution. However, they are much easier to derive and easier to work with. They have the added advantages that a reader can tell with a glance approximately how the original integral behaves under changing conditions and no numerical computations need to be done. Hence it is desirable to seek useful approximations for ω_h in Equation (51).

The Miller and Abrahams^{17b} treatment of the resistivity assumed that $G(\Delta)$ was sharply peaked near $\Delta=0$. In other words, it was assumed that in the impurity ensemble, the arrangement of atoms was such that most energy differences between donor ground states were close to the value $\Delta=0$. However, this assumption was somewhat arbitrary on the part of Miller and Abrahams since they did not specifically calculate the $G(\Delta)$ function. Before using the methods of a similar approximation to evaluate ω_h , one should determine under what conditions it may be valid in the present calculation since a function for $G(\Delta)$ is now available in Equation (43).

It shall be shown here that the criterion for the approximation that $G(\Delta)$ is sharply peaked at $\Delta=0$ is that the compensation ratio must be small. One would expect this intuitively since a low compensation implies a low number of acceptors. This, in turn, implies that the perturbation of the acceptor coulomb field on a typical donor ground state is small. Hence, most of the differences in energy Δ between the various donor ground states would have values close to $\Delta=0$. A quantitative statement of the low compensation approximation may be derived by initially determining how $G(\Delta)$, which appears to be slowly varying in Equation (43), can be considered sharply peaked at $\Delta=0$. This is done by showing that the difference between the limits $(\Delta^+ - \Delta^-)$ must be made smaller than $k_B T$ and that the average value of Δ is, in many cases, zero. Then an inequality for K as a function of N_D and T may be obtained which shows how low the compensation must be for the above criteria to be met.

Because of the limits on $G(\Delta) = e^2/2k_0 E^2 r (1-\Delta/E)^3$, the average value of Δ is not zero in the integral over the upper range (i.e., $e^2/k_0 E < r < \infty$) in Equation (51). That is, for $e^2/k_0 E < r < \infty$

$$\int_{\Delta^-}^{\Delta^+} G(\Delta) \Delta d\Delta = E - e^2/k_0 r \quad . \quad (57a)$$

Hence, one certainly cannot consider $G(\Delta)$ peaked near $\Delta=0$ in this case. And although the average value of Δ is zero for the lower range ($0 < r < e^2/k_0 E$) since in this case

$$\int_{\Delta^-}^{\Delta^+} G(\Delta) \Delta d\Delta = 0 \quad , \quad (57b)$$

it would appear that one could not consider Δ to have an average value of zero in general. However this integral over the lower range in Equation (51) is the only one of interest for the following reasons. Unless the parameter $e^2/k_0 E$ is of the order of the transverse Bohr radius a or smaller, the integral over the upper range of r is very small compared with the one over the lower r range because of the factor $\exp(-2r/a)$. Furthermore, even though the upper range r integral is larger than the lower range one when $E > e^2/k_0 a$, the $1/E^4$ dependence in the density of states makes energies this large extremely improbable and consequently shows that the term with the density of states times the large r integral can be neglected for large E . That is, the probability that E is in the range $e^2/k_0 a < E < \infty$ is

$$\int_{e^2/k_0 a}^{\infty} F(E) dE = 1 - \exp\left[-\left(\frac{E_A}{e^2/k_0 a}\right)^3\right] \approx \left(\frac{a}{R_A}\right)^3 . \quad (58)$$

For N_A less than $2.7 \times 10^{17} \text{ cm}^{-3}$ in silicon and N_A less than $1.1 \times 10^{16} \text{ cm}^{-3}$ in germanium, this probability is less than 1%.

Hence, unless K is of the order of unity for donor concentrations that exhibit narrowing, the second half of the right side of Equation (51) is small in comparison with the first for large or small E and may be dropped. Thus, Equation (57b) allows one to always consider to have an average value of zero.

Secondly, one may determine how $G(\Delta)$ can be considered sharply peaked by initially noting that finite values for $G(\Delta)$ are attained only between the limits Δ^- and Δ^+ [see Equation (43)]. Thus, if the limits are close together, near $\Delta=0$, then $G(\Delta)$ takes on a sharply peaked character at that value. How close together the limits need to be is determined by how rapidly varying the function of Δ being averaged is. Inspection of Equation (51) shows that $\Delta/[1+\exp(-\beta(E-\Delta-\zeta_g))][1-\exp(-\beta\Delta)]$ varies slowly with Δ if Δ is small in relation to $k_B T$. So if the width of the entire range of Δ is less than $k_B T$, one is assured that he can consider $G(\Delta)$ sharply peaked. The relevant criterion is thus

$$(\Delta^+ - \Delta^-) = \frac{2E}{\frac{e^2}{k_0 \epsilon r} - \frac{k_0 r E}{e^2}} \ll k_B T . \quad (59a)$$

It turns out that the compensation must also be low to satisfy this condition.

To obtain a quantitative form of Inequality (59a) in the low T limit (i.e., $T \ll T_e$, as given by Inequality (29b)) one should inspect Equation (51). From the $r^{7/2} \exp(2r/a)$ function one may conclude that most transitions occur between donors separated by a distance of the order of a . Furthermore, if the temperature is low, most transitions occur between donors with energies very close to ζ_g , the approximate peak of the product of the electron distribution functions in Equation (51). Inserting the low T value of $\zeta_g = E_A / [-\ln(1-K)]^{1/3}$ for E and assuming a value of $3a$ for r in Inequality (59a), one may determine a typical low T value for $(\Delta^+ - \Delta^-)$ to be

$$(\Delta^+ - \Delta^-) = \frac{2\zeta_g}{\frac{e^2}{3k_0 a \zeta_g} - \frac{3k_0 a \zeta_g}{e^2}} \approx \frac{6E_A^2 k_0 a}{e^2 [-\ln(1-K)]^{2/3}} \ll k_B T \quad (59b)$$

Since Inequality (29b) must hold at low T, combination of it with Inequality (59b) yields

$$K^{1/3} [-\ln(1-K)]^{2/3} \ll \frac{R_D}{63.6 a}$$

or, if K is not close to unity,

$$K \ll \frac{R_D}{63.6 a} \equiv K_c \quad (59c)$$

Thus, at temperatures lower than T_c , if the compensation is lower than K_c , then $(\Delta^+ - \Delta^-)$ is small and $G(\Delta)$ can be considered sharply peaked near $\Delta=0$. Since K_c decreases with increasing N_D , one can find the lowest relevant value for K_c by choosing the upper limit

of N_D in the region of N_D where line narrowing is observed, i.e., $2 \times 10^{17} \text{ cm}^{-3}$ in Ge and $3 \times 10^{18} \text{ cm}^{-3}$ in Si. (Above these concentrations the line broadens;^{5,9,12,13} consequently such concentrations are not germane to the present problem). Thus, one obtains for germanium $K_C = 2.8 \times 10^{-2}$ and for silicon $K_C = 3.2 \times 10^{-2}$ as the upper limit on K useable in the low K approximation at low temperatures.

One may also obtain an upper limit on the compensation for the case when the temperature is high (i.e., $T \gg T'_C$ as given by Inequality (32b)). Again inspecting Equation (51), one finds that for high T, most transitions occur between donors with energies $E = E_0 = (3/4)^{1/3} E_A$, the peak of the density of states. Inserting E_0 for E in Inequality (59a) and again assuming 3a for r, one finds that a typical value for $(\Delta^+ - \Delta^-)$ at high temperatures is

$$(\Delta^+ - \Delta^-) \approx \frac{6 \left(\frac{3}{4}\right)^{2/3} E_A^2}{e^2/k_0 a} \ll k_B T \quad . \quad (59d)$$

Consequently, the inequality for K at high T is

$$K \ll 9.07 \times 10^{-2} \left(\frac{R_D}{a}\right)^3 \left(\frac{k_B T}{e^2/k_0 a}\right)^{3/2} \equiv K'_C \quad . \quad (59e)$$

Thus, if the compensation is lower than K'_C , then $G(\Delta)$ can be considered sharply peaked for high temperatures. (For Ge with $N_D = 2 \times 10^{17} \text{ cm}^{-3}$, $K'_C = 2.2 \times 10^{-4} T^{3/2}$ and for Si with $N_D = 3 \times 10^{18} \text{ cm}^{-3}$, $K'_C = 4.1 \times 10^{-5} T^{3/2}$.) However since the temperature must be high, Inequality (59e) shows that K'_C must be larger

than K_c for the same sample. This means that Inequality (59e) will be valid, if Inequality (59c) is valid. Thus, Inequality (59c) gives the low K condition for either high or low T.

One can now compute ω_h in the low K approximation by applying the sharply peaked condition on $G(\Delta)$ to the first term on the right hand side of Equation (51). Removing the electron distribution function of vacant donors and the phonon energy distribution times Δ from the Δ integral, evaluating these functions at $\Delta=0$, and integrating $G(\Delta)$ (the integral of which is normalized to unity), one obtains

$$\omega_h = \frac{1}{B(1-K)} \int_0^{\infty} dE \frac{3E_A^3}{E^4} \frac{\exp[-(E_A/E)^3]}{[1+\exp(\beta(E-\zeta_g))][1+\exp(-\beta(E-\zeta_g))]} \times 4\pi N_D \int_0^{e^2/k_0 E} dr r^{7/2} \exp(-2r/a) . \quad (60)$$

The integral over r is found to be proportional to $[\Gamma(9/2) - \Gamma(9/2, e^2/k_0 Ea)]$. However, the second term in this expression is small since, for high T, the parameter inside the incomplete gamma function is approximately the large ratio $e^2/k_0 E_0 a = 1.1R_A/a$ and, for low T, it is approximately the large ratio $e^2/k_0 E_D a = R_D/a$. Thus the expression for the hopping frequency is

$$\omega_h = \frac{4\pi N_D}{B(1-K)} \left(\frac{a}{2}\right)^{9/2} \Gamma\left(\frac{9}{2}\right) k_B T \int_0^{\infty} dE \frac{3E_A^3 \exp[-(E_A/E)^3]}{E^4 [1+\exp(\beta(E-\zeta_g))][1+\exp(-\beta(E-\zeta_g))]} . \quad (61)$$

Equation (61) is the average hopping frequency for all temperatures in the limit that the compensation is low.

2. The Low Temperature and High Temperature Approximations

The average hopping frequency in Equation (61) may be calculated either by numerical techniques or by further approximations. Since Equation (61) has only one restriction, that K be well below K_C , and yet since it involves only one integration, it is well worth ones while to attempt a numerical calculation of ω_h with the methods discussed in Appendix C. Furthermore, since it is possible to numerically calculate ζ_g and ω_h in one step (see Appendix C), the value of ω_h may be determined as accurately as possible for any Π_D , T , and $K \ll K_C$, without an approximation for the Fermi energy. The results of a numerical calculation on hypothetical samples of arsenic-doped germanium are discussed in the next part of this section. Alternatively, an attempt to reduce ω_h to a closed form algebraic expression may also be done. Since Equation (61) is valid for high or low temperatures, the expression for ω_h may be simplified by using the same high and low T approximations used to derive the expressions for ζ_g in Equation (34) and (31), respectively.

Upon examining Equation (61), one finds that the product of the two electron distribution functions may be considered slowly varying, if an inequality similar to Inequality (32b) holds, that is, if $T \gg T'_C \approx 0.66E_A/k_B$. This then allows one to consider $F(E)$ sharply peaked at E_0 , remove the other functions of E from the integral, evaluate them at $E=E_0$, and integrate $F(E)$. The result of this process is

$$\omega_h = \frac{DN_D}{B(1-K)} (k_B T) \left[\frac{1}{1+\exp(\beta(E_0 - \zeta_g))} \right] \left[\frac{1}{1+\exp(-\beta(E_0 - \zeta_g))} \right], \quad (62)$$

where $D=4\pi(a/2)^{9/2}\Gamma(9/2)$. If the high temperature ζ_g from Equation (34) is inserted into Equation (62), this becomes

$$\omega_h = \frac{DN_D}{B} (k_B T) K = \frac{DN_A}{B} (k_B T) . \quad (63)$$

Hence, for low K and high T , ω_h is a linear function of T with slope $Dk_B N_A/B$. It is also important to note that the average probability of a transition is simply proportional to N_A , the number of acceptors. As the number of acceptors is reduced, one would expect intuitively that ω_h should approach zero because there are fewer vacant sites available for a hop. Equation (63) is consistent with that expectation. This dependence of ω_h upon compensation, while expected, has never appeared in any previous expression for ω_h .^{4,5,9,10,13}

Finally, one may derive the low T dependence of Equation (61) by considering the electron distribution functions in Equation (61) to be sharply peaked at $E=\zeta_g$, integrating over E , and inserting the low temperature ζ_g given by Equation (30). One obtains with this procedure

$$\omega_h = \frac{3D N_D}{B} \frac{(k_B T)^2}{E_D} K . \quad (64)$$

The important point to note here is that the linear K dependence in this approximation is similar to the linear K dependence in the high T approximation, Equation (63). Apparently ω_h varies fairly

linearly with K for any range of temperature, if the compensation is low. There is no guarantee, however, that this linear K dependence would continue for K higher than K_c . To study ω_h for $K \gg K_c$, one would have to return to the exact solution, Equation (51), and evaluate it directly.

F. RESULT OF NUMERICAL AND ANALYTIC CALCULATIONS--EXAMPLE IN Ge(As)

To obtain an idea of how ω_h depends upon N_D , T and K and to see how well Equations (63) and (64) approximate ω_h , both numerical and analytic calculations were done using parameters relevant to arsenic-doped germanium. To study the donor concentration dependence, it was assumed that one had two sets of Ge(As) samples at $T=4^\circ\text{K}$. In one set all the samples were assumed to have the same concentration of acceptors, $N_A = 5 \times 10^{13} \text{ cm}^{-3}$. In the second set the samples were allowed to have different N_A , but only under the condition that each sample had the same compensation ratio, $K = 1.087 \times 10^{-3}$. In both sets, N_D ranged from $1.08 \times 10^{18} \text{ cm}^{-3}$ to $2.11 \times 10^{15} \text{ cm}^{-3}$ ($1 < R_D/a < 8$). (Note that the constant N_A and constant K were chosen so that a sample with $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$ would be a member of both sets.) It is not certain which case, constant N_A or K (if either one), occurs in actual sets of samples, which are grown from the same germanium melt, but not deliberately compensated. Hence, both cases were examined in the calculation.

The resulting plot of the average transition rate of hopping electrons vs. R_D/a as calculated numerically from Equation (61) is shown for both sets of samples in Figure 8 (solid lines). Also

Figure 8. Plot of the theoretical $\log \omega_h$ vs. R_D/a for arsenic-doped germanium at 4°K. Note the difference in R_D dependence between the assumption of constant N_A and the assumption of constant K . Solid curves are the numerical solutions for low K [Equation (61)] and dot-dashed lines are the low K , low T analytic solutions of Equation (64).

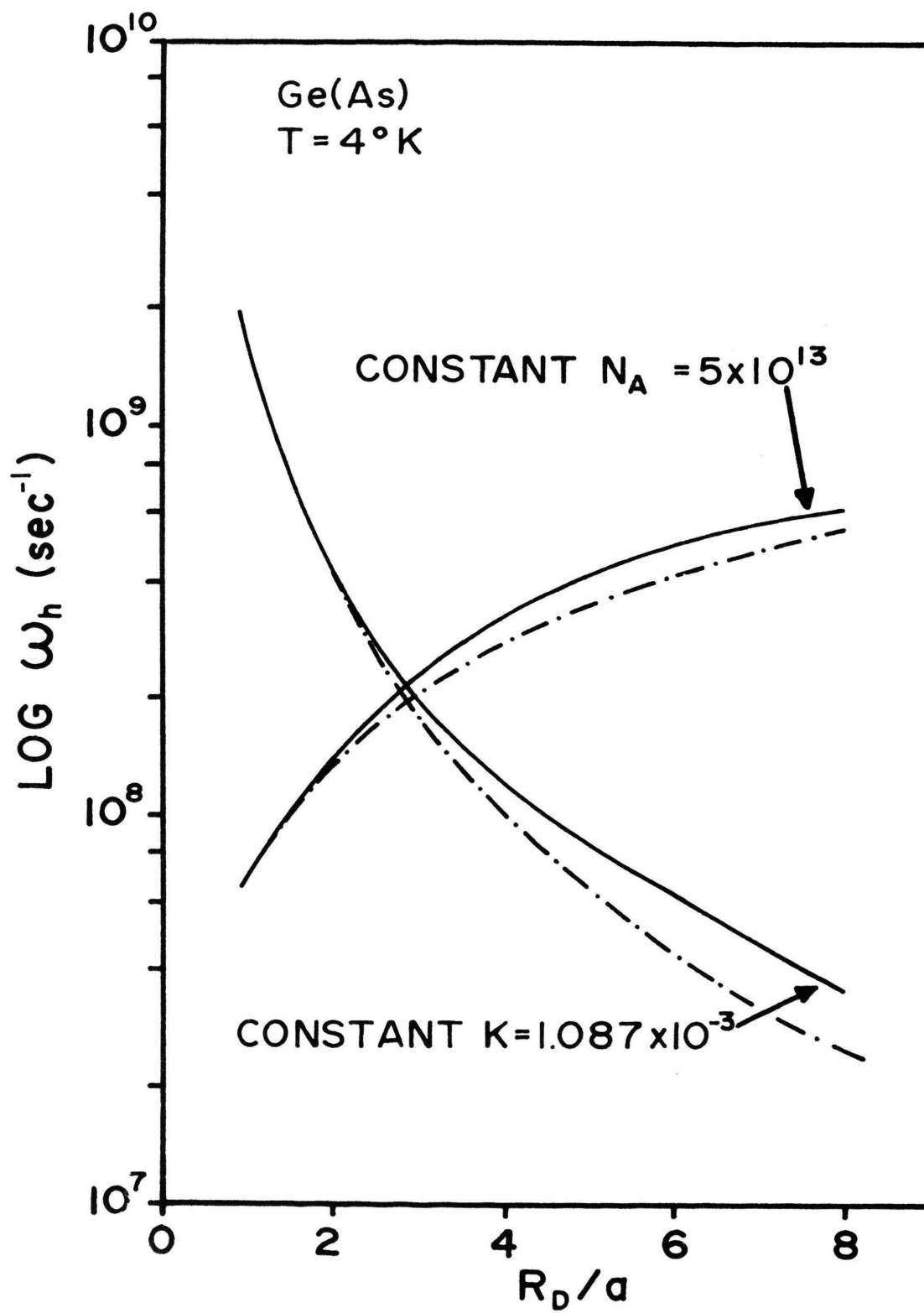


Figure 8

shown are the low T approximation curves, (dot-dashed lines), calculated from Equation (64). As shown in Figure 8 the low T approximation for ω_h is a very good approximation for low R_D/a (high N_D) and remains fairly good throughout the region investigated. It begins to fail for high R_D/a (low N_D) because the 4°K temperature does not satisfy Inequality (29b) for low N_D . These plots also show that assuming constant N_A causes ω_h to decrease with decreasing R_D (or with increasing N_D) while assuming constant K causes ω_h to increase with decreasing R_D . Equation (64) shows that for low T the constant N_A dependence is approximately $\omega_h \propto R_D$ and the constant K dependence is $\omega_h \propto 1/R_D^2$.

Such interesting results can be explained physically by showing that the assumption of constant K or N_A affects the N_D dependence of the number of available vacant donors (holes) to which an electron can hop, which in turn affects ω_h . Essentially Equation (16) states that the hopping frequency of an electron is approximately equal to the transition rate to a single vacant donor times the total number of available vacant donors. Now if Δ is small and T is low, the number of holes available for transition is equal to the number of holes with ground state energies in the region where the product distribution of electrons and holes has a significant value, i.e. in the region $(\zeta_g - k_B T) \lesssim E \lesssim (\zeta_g + k_B T)$. Hence, the number of available vacant donors is simply N_D times the density of states at ζ_g , all times $2 k_B T$. But, at low T and K, $\zeta_g = E_D$ and $F(\zeta_g) = F(E_D) \approx 3E_A^3/E_D^4$. So

$$\begin{aligned}
 \omega_h &\propto \# \text{ available holes} \\
 &\propto 2N_D F(\zeta_g) k_B T \\
 &\approx 6N_D E_A^3 k_B T / E_D^4 .
 \end{aligned}$$

Thus,

$$\omega_h \propto N_A R_D = (3/4\pi)^{1/3} N_A / N_D^{1/3} \quad (65a)$$

or

$$\omega_h \propto K / R_D^2 = (4\pi/3)^{2/3} N_D^{2/3} K . \quad (65b)$$

If N_A is constant, then the numbers of available holes depends only on the value of the density of states at $E=E_D$. Since $F(E)$ decreases with increasing E and since E_D increases as R_D decreases (as N_D increases), the number of available holes decreases with decreasing R_D . Hence, ω_h also decreases as R_D decreases if N_A is assumed constant; as shown in the first result of the above expression, ω_h is proportional to R_D . On the other hand, if K is constant, the number of available holes also depends on the fact that decreasing R_D (increasing N_D) creates new holes to keep K fixed. The R_D dependence of this creation of new available holes ($1/R_D^3 \propto N_D$) is more rapid than the decrease due to the density of states. Hence, ω_h increases as R_D decreases (or N_D increases) for constant K and is proportional to $1/R_D^2$ as shown in the second result of the above expression.

The temperature dependence of ω_h can also be studied. In this case, each set of Ge(As) samples were chosen to have four donor

concentrations: (1) $N_D = 3.4 \times 10^{16} \text{ cm}^{-3}$; (2) $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$; (3) $N_D = 7.0 \times 10^{16} \text{ cm}^{-3}$; and (4) $N_D = 1.8 \times 10^{17} \text{ cm}^{-3}$. Plots of the average hopping frequency vs. the temperature for the constant N_A set and the constant K set are shown in Figures 9(a) and 9(b) respectively. Also shown on both plots are the low T and high T approximations for the hypothetical sample with $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$. [Recall that this sample is the same in the constant K and the constant N_A sets. Hence curves 9(a2) and 9(b2) are identical as are the approximate curves. Note, in addition, that in Figure 9(a) the dashed line is the high T approximation for all curves on that graph since N_A is constant [see Equation (63)]}. The low T curve is a good approximation for T less than or of the order of 8°K. In addition, the steepness of the ω_h vs. T curves as a function of N_D reflects the earlier mentioned point that ω_h decreases with increasing N_D for N_A constant and increases with increasing N_D for K constant. More importantly, however, the ω_h vs. T curves all go to zero as T approaches zero, a point shown earlier for the formal expression of ω_h , Equation (51). For low temperatures, the low compensation ω_h is proportional to T^2 , as shown in Equation (64). Physically, the T^2 comes from two factors of T, each of which originate from two different sources. One source is the phonon involvement described by the $\Delta/[1-\exp(-\beta\Delta)]$ factor which reduces to $k_B T$ in the low K approximation. The other source is from the product distribution of electrons and holes discussed in the last paragraph.

Finally, the K dependence of ω_h was studied by considering a single set of hypothetical samples at $T=4^\circ\text{K}$ with $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$. Then, K was assumed to vary from zero to the value

Figure 9. Plot of the theoretical ω_h vs. temperature for arsenic-doped germanium samples of varying concentration. Graph (a) is for constant N_A and Graph (b) is for constant K . The solid curves are the numerical solutions for low K

[Equation (61)]. In each graph the various curves are for

- (1) $N_D = 3.4 \times 10^{16} \text{ cm}^{-3}$,
- (2) $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$,
- (3) $N_D = 7.0 \times 10^{16} \text{ cm}^{-3}$, and
- (4) $N_D = 1.8 \times 10^{17} \text{ cm}^{-3}$.

The dashed line on each graph is the low K , high T approximation [Equation (63)] for Curve (2), $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$.

The dot-dashed line on each is the low K , low T approximation [Equation (64)] for Curve (2).

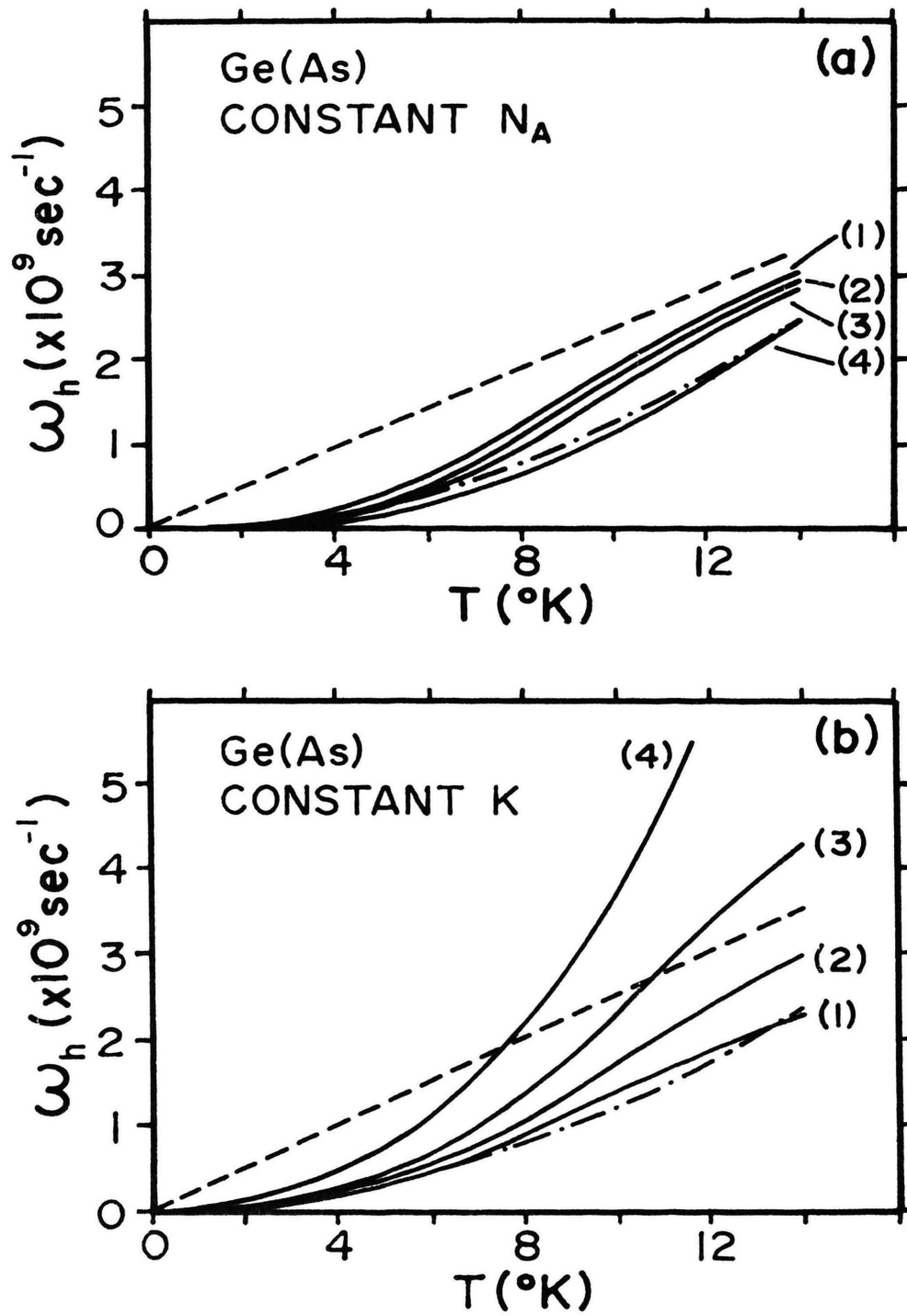


Figure 3

$K_c = 4.56 \times 10^{-2}$ for the various samples within the set. The resulting numerical ω_h vs. K curve is plotted in Figure 10 (solid line). The drawing shows that for low K , that the low T approximation (Equation (64)) is a very good approximation for chosen N_D , T and K values. The physical interpretation of this linear K dependence is that the probability of an electron hopping to another donor should be approximately proportional to the number of available vacant donors N_A , which is proportional to K , for constant N_D .

Figure 10. Plot of the theoretical ω_h vs. the compensation ratio for a Ge(As) sample with $T=4^\circ\text{K}$ and $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$. Such linear K dependence by ω_h , at low K , has not been predicted by previous theories.

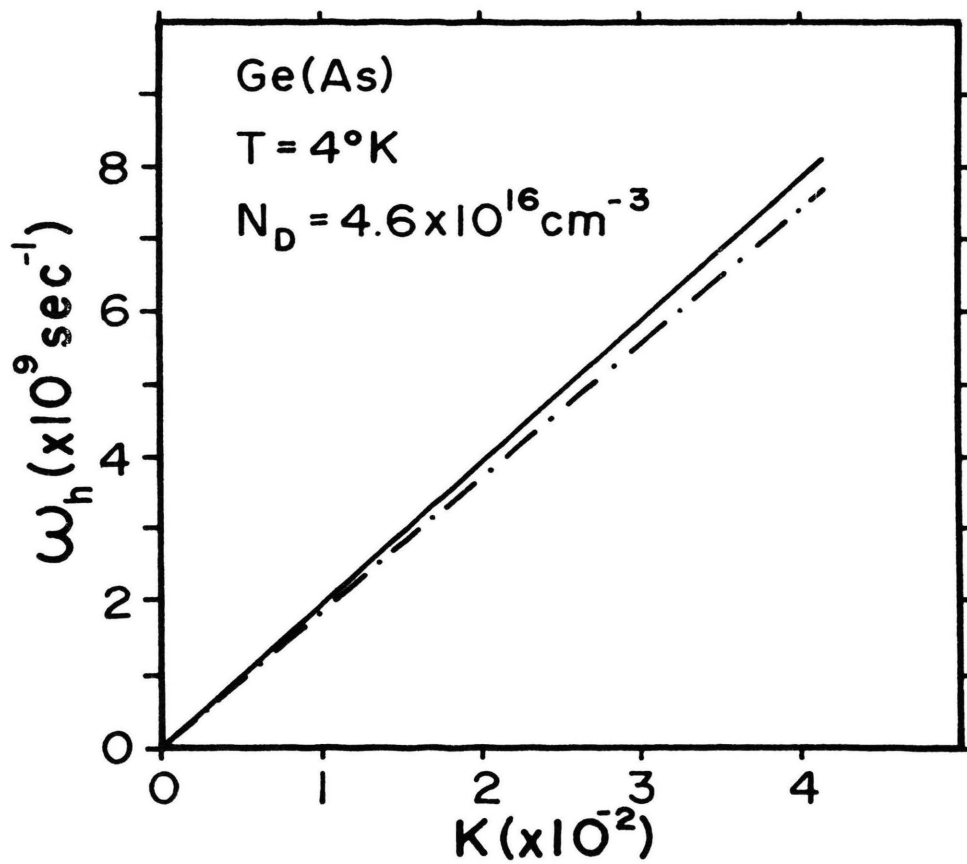


Figure 10

IV. CALCULATION OF $\langle H^2 \rangle_{\text{ave}}$

Now that the calculation of ω_h is complete, one final computation is necessary before the narrowed line breadth may be predicted from Equation (3). The exact form for $\langle H^2 \rangle_{\text{ave}}$ must be determined. As shown in Appendix B $\langle H^2 \rangle_{\text{ave}}$ corresponds to the mean square spread of the non-narrowed magnetic field spectrum from its center. This average is determined by integrating that spectrum as over a normalized probability distribution $P(H)$ which describes the shape of the non-narrowed spectrum. For convenience the center of $P(H)$ is chosen to be $H=0$. The particular spectral distribution of interest here is the ESR spectrum of localized donor electrons consisting of $n=2I+1$ Gaussian lines. These lines are assumed to be equal in strength and of the same Gaussian shape, each having a mean square spread of ΔH_0 , and spaced at regular intervals of $2H_0$ (see Figure 1a). With the above information a normalized distribution for this spectrum can be written as

$$P(H) = \sum_{\substack{m=-(n-1) \\ (m \text{ odd})}}^{(n-1)} \frac{1}{n\sqrt{2\pi} \Delta H_0} \exp \left[-\frac{(H-mH_0)^2}{2(\Delta H_0)^2} \right]. \quad (66)$$

Thus, $\langle H^2 \rangle_{\text{ave}}$ is

$$\langle H^2 \rangle_{\text{ave}} \equiv \int_{-\infty}^{\infty} H^2 P(H) dH \quad (67a)$$

$$= \frac{1}{n\sqrt{2\pi} \Delta H_0} \sum_{\substack{m=-(n-1) \\ (m \text{ odd})}}^{(n-1)} \int_{-\infty}^{\infty} dH H^2 \exp \left[-\frac{(H-mH_0)^2}{2(\Delta H_0)^2} \right] \quad (67b)$$

$$= \frac{1}{n} \sum_{\substack{m=-(n-1) \\ (m \text{ odd})}}^{(n-1)} [(\Delta H_0)^2 + m^2 H_0^2] \quad (67c)$$

$$= (\Delta H_0)^2 + \frac{2}{n} \sum_{m=1,3,5,\dots}^{(n-1)} m^2 H_0^2 \quad (67d)$$

The summation over m can be changed to a sum over both even and odd integers and then evaluated. The result is

$$\sum_{m=1,3,5,\dots}^{n-1} m^2 = \sum_{j=1}^{n/2} (2j-1)^2 = \frac{n}{2} \left[\frac{n^2-1}{3} \right] \quad (68)$$

Inserting Equation (68) into Equation (67d) and substituting $n=2I+1$, one obtains

$$\langle H^2 \rangle_{\text{ave}} = (\Delta H_0)^2 + \frac{4}{3} I(I+1) H_0^2 \quad (69)$$

Table I shows values of ΔH_0 and H_0 obtained from data in References 1 and 4 along with other pertinent information on isolated donor ESR spectra in silicon and germanium. Table II gives the values of $\langle H^2 \rangle_{\text{ave}}$ for these donors computed from Equation (69) and the resulting numerator of Equation (3) needed in the computation of ΔH . In most cases the $(\Delta H_0)^2$ term can be neglected except for donors with $I=\frac{1}{2}$.

With $\langle H^2 \rangle_{\text{ave}}$ computed, one may now compare its value with the previous value of ΔH_{hfs}^2 used by others (see Equations (6)). Since the total hyperfine structure is given by

$$\Delta H_{\text{hfs}} = 4IH_0 \quad (70)$$

Table I. Data on the non-narrowed ESR spectra of various donor impurities.

Table I

(a) Germanium ⁴					
Doping Element	As	Bi	P	Sb ^a	
I	3/2	9/2	1/2	5/2 or 7/2	
Number Lines	4	10	2	14	
g	1.5700±.0002	1.5671±.0004	1.5631±.0002	1.60	
ΔH_0	5.5±0.5	5.0±0.5	5.0±1	--	
H_0	17.9	52.4	10.5	--	
N_D (cm ⁻³)	5 x 10 ¹⁵	5 x 10 ¹⁵	8 x 10 ¹⁴	5 x 10 ¹⁵	

(b) Silicon ¹					
Doping Element	As	Bi	P	Sb ¹²¹	Sb ¹²³
I	3/2	9/2	1/2	5/2	7/2
Number Lines	4	10	2	6	8
g	1.99837	2.0003	1.99850	1.99858	1.99858
ΔH_0	1.6	2.2	1.4	1.3	1.3
H_0	35.3	--	21	34.5 ^b	19 ^b
N_D (cm ⁻³)	1.8x10 ¹⁶	2x10 ¹⁶	1.5x10 ¹⁶	4x10 ¹⁷	4x10 ¹⁷

^aNon-narrowed spectrum not observable in Ge(Sb) because of strain broadening effects.⁴

^bC. Kittel, Introduction to Solid State Physics (John Wiley & Sons, New York, 1971), 4th ed., p. 593. The Sb isotopes are observed simultaneously. Their abundances are Sb¹²¹ (56%) and Sb¹²³ (44%).

Table II. Calculated values of crucial parameters needed to predict the line breadth and the lower bound on ω_{\min} .

Table II

(a) Germanium				
	<u>As</u>	<u>Bi</u>	<u>P</u>	
$\langle H^2 \rangle_{\text{ave}} (0_e^2)$	1.63×10^3	9.05×10^4	135	
$\frac{g \mu_B \langle H^2 \rangle_{\text{ave}}}{\hbar} (0_e/\text{sec})$	2.25×10^{10}	1.25×10^{12}	1.86×10^9	
$\omega_{\text{min}} (\text{sec}^{-1})$	5.58×10^8	4.16×10^9	1.60×10^8	
(b) Silicon				
	<u>As</u>	<u>P</u>	<u>Sb¹²¹</u>	<u>Sb¹²³</u>
$\langle H^2 \rangle_{\text{ave}} (0_e^2)$	6.23×10^3	443	1.39×10^4	7.57×10^3
$\frac{g \mu_B \langle H^2 \rangle_{\text{ave}}}{\hbar} (0_e/\text{sec})$	2.19×10^{11}	1.56×10^{10}	4.90×10^{11}	1.33×10^{11}
$\omega_{\text{min}} (\text{sec}^{-1})$	1.39×10^9	3.70×10^8	2.08×10^9	1.53×10^9

the ratio of ΔH_{hfs}^2 to Equation (69) is about

$$\frac{\Delta H_{\text{hfs}}^2}{\langle H^2 \rangle_{\text{ave}}} \approx \frac{12I}{I+1} \quad (71)$$

or 4.00, 7.20, and 9.82 for phosphorus, arsenic and bismuth donors, respectively. Thus, a point stated earlier has now been shown. Namely, that the original assumption of $\langle H^2 \rangle_{\text{ave}} = \Delta H_{\text{hfs}}^2$ would yield line breadths a little less than an order of magnitude too high when used with Equation (3).

Finally, Equation (3) can only be used when the narrowing is strong, that is, when ω_h is rapid. The condition is expressed by the inequality

$$\omega_h \gg \omega_{\text{min}} = \frac{g \mu_B [\langle H^2 \rangle_{\text{ave}}]^{1/2}}{\hbar} \quad (72)$$

$$= \frac{g \mu_B [\Delta H_0^2 + \frac{4}{3} I(I+1)H_0^2]^{1/2}}{\hbar} \quad (73)$$

given in the discussion of Equation (3) and in Appendix B. When ω_h is much less than this value, the narrowing is weak and a spectrum similar to the non-narrowed one should be observed. Table II gives the computed values of ω_{min} for the various donors.

V. DISCUSSION OF THEORY AND EXPERIMENTS ON ESR LINE NARROWING

There are many papers⁴⁻¹³ which have presented data on donor ESR line widths in semiconductors. However, these authors compared the influence of phonon-induced tunneling to their data using incorrect expressions for ω_h and $\langle H^2 \rangle_{ave}$ needed in Equation (3). Hence the conclusions based upon such comparisons are in doubt. To correct the situation, the new expression for ΔH will be presented in this section and then compared with previous expressions used for ΔH (or ω_h). Next the new expression will be compared with data published by these authors, their conclusions will be analyzed, and further conclusions will be drawn. Finally, an experiment will be proposed which will hopefully decide whether or not hopping is influencing the donor ESR spectra in Group IV semiconductors.

A. COMPARISON WITH PREVIOUS THEORIES

The new theoretical expression for the width between the inflection points on the narrowed line shall be called ΔH_{THEORY} to distinguish it from the experimental values ΔH_{EXP} . The expression may be obtained by first noting that the narrowed line has a Lorentzian shape when the field is along the [100] axis⁴, which is true for all the experiments considered in this section. For a Lorentzian function the ratio of the width at half-maximum to the width between the inflection points is¹⁰ $\sqrt{3}$. Since ΔH in Equation (3) is the half-width at half-maximum, one has

$$\Delta H = \frac{\sqrt{3}}{2} \Delta H_{THEORY} \quad . \quad (74)$$

Combining Equations (3), (69), and (74) one obtains

$$\Delta H_{\text{THEORY}} = \frac{2}{\sqrt{3}} \frac{g\mu_B [\Delta H_0^2 + \frac{4}{3} I(I+1)H_0^2]}{\omega_h} . \quad (75)$$

Because most samples tested to date were uncompensated (i.e., not deliberately compensated) and thus the compensation ratio should be low, the expression used for ω_h in this section will be considered only in the low K approximation. Then, ω_h has the form given in Equation (61) or

$$\omega_h = \frac{D}{B(1-K)} N_D (k_B T) \int_0^\infty \frac{dE \ 3E_A^3 \exp[-(E_A/E)^3]}{E^4 [1+\exp(\beta(E-\zeta_g))][1+\exp(-\beta(E-\zeta_g))]} . \quad (61)$$

The asymptotic form at low T for Equation (61) is Equation (64) or

$$\omega_h = \frac{3D}{B} K N_D \frac{(k_B T)^2}{E_D} \quad T \ll T_c . \quad (64)$$

The asymptotic form for high T [Equation (63)] is

$$\omega_h = \frac{D}{B} K N_D (k_B T) \quad T \gg T_c . \quad (63)$$

The new Equation (75) for ΔH_{THEORY} differs markedly from that used in References 4 and 5, i.e., Equation (6). The major difference is between their expression for ω_h ,

$$\omega_h = U_{ij}(R_D, \Delta) = \frac{1}{B} R_D^{3/2} \exp(-2R_D/a) \frac{\Delta}{1-\exp(-\beta\Delta)} \quad (76)$$

and the new expression for ω_h given above in Equation (61). First note the difference in the donor concentration dependence. The new expression is approximately proportional to N_D (or $1/R_D^3$) while the old one falls off much faster with R_D because of the nearly exponential dependence. The difference is caused mainly by the integration over the donor distribution function. One might suppose, erroneously, that this less drastic R_D dependence is due to the fact that hopping to other than nearest neighbors was taken into account. However, if only transition to other than nearest neighbors is taken into account, ω_h would fall off with R_D at an even slower rate than $1/R_D^3$, in worse agreement with Equation (76) than when all donors are included. (This fact can be shown by comparing the distribution function for nearest neighbors, Equation (8a), to the total distribution $3r_{ij}^2/R_D^3$ used to derive ω_h . For a given r_{ij} , Equation (8a) falls off slower with increasing R_D than the latter expression.) Thus the R_D dependence in Equation (76) is not that exhibited by the hopping frequency derived with the Miller and Abrahams methods.

The second difference between Equations (61) and (76) is in the temperature dependence. Because of the Miller and Abrahams low K approximation, the phonon influence on ω_h , via the term $\Delta/[1-\exp(-\beta\Delta)]$, has become a $(k_B T)$ factor in front of the integral in Equation (61). In addition, there is a temperature dependence from the electron distribution, which contributes a factor of $3k_B T/E_D$ at low temperatures. Thus, ω_h goes to zero as T goes to zero, unlike the old $\omega_h = U_{ij}(R_D, \Delta)$ for positive Δ . This property of ω_h will be important when the experimental data is analyzed.

Thirdly, a new factor has appeared in the hopping frequency which has never appeared in any previous expression for ω_h . This is the compensation dependence arising because of the electron distribution functions (shown better in Equation (63) or (64)). Thus, the compensation ratio K is a third measurable parameter, besides T and N_D , which can be used to compare the effect hopping should have on the ESR spectrum, as one intuitively expects.

Comparison can also be made between Equation (61) and the expressions for the hopping frequency used in Reference 10, where

$$\omega_h = U_{ij}(R_D, -\epsilon_3) \propto R_D^{3/2} \exp(-2R_D/a) \frac{\epsilon_3}{\exp(\beta\epsilon_3)-1} \quad (77)$$

or in Reference 13, where

$$\omega_h \propto \frac{1}{\exp(\beta\epsilon_i)-1} \quad (78)$$

These expressions depend on some activation energy, which does not appear in Equation (61). Furthermore, the temperature dependence of Equations (77) or (78) could easily be incorrect because it is strongly influenced by the choice of activation energy. Also, the electron distribution functions contribute an additional temperature dependence to ω_h which is not expressed.

Thus, it is clear that the expression for ω_h , Equation (61), obtained with the Miller and Abrahams techniques, bears little resemblance to the previous expressions used for the hopping frequency, i.e., Equations (76), (77), and (78).

B. COMPARISON WITH EXPERIMENTAL DATA

The most striking result one notices upon combining Equations (75) and (61) is that, for constant temperature and compensation, ΔH_{THEORY} should be approximately proportional to R_D^3 . Yet Wilson's⁴ data (see Figure 4(a)) shows that ΔH_{EXP} actually has an $\exp(R_D/R_0)$ dependence, where R_0 depends upon the doping element. Thus, while the old theory of the donor concentration dependence of narrowing by hopping roughly agreed with experiment (see Section II), the new, more accurate theory of hopping does not agree at all. Hence, since the expected R_D^3 dependence is not observed in the data, it seems that the previous conclusion of Reference 4 that hopping causes the variation of ΔH_{EXP} with donor concentration is probably mistaken.

One might attempt to resolve the matter by noting that the compensation K might not be constant in the samples. (Wilson did not mention values for this parameter.) It might happen that if K were allowed to vary, this variation might account for the seeming failure of motional narrowing by hopping to explain the N_D dependence in ΔH_{EXP} . If the compensation is allowed to increase with N_D such that $K \propto R_D^3 \exp(R_D/R_0)$, then the data can be fit. However, there is no physical reason to adjust K in this manner. In fact, there is strong evidence against doing so since Wilson's samples were not deliberately compensated. Thus, any acceptor atoms in the samples would presumably have come from impurities in the germanium prior to doping. Impurities in the doping element are much fewer since the concentration of the doping element is many orders of magnitude below the germanium

concentration in the samples. Hence, if the samples came from the same germanium melt, they would all have the same concentration of acceptors. As N_D increases, then, the compensation ratio N_A/N_D would be expected to decrease, not increase. Hence, the ability of narrowing by hopping to explain the donor concentration dependence still remains in serious doubt.

The other important dependence observed in ΔH_{EXP} is a temperature dependence. To study this function of T , it is convenient to convert the ΔH_{EXP} data to frequency values ω_N , where ω_N is defined as the experimentally observed narrowing frequency and calculated from experimental data as

$$\omega_N = \frac{\frac{2}{\sqrt{3}} g \mu_B [\Delta H_0^2 + \frac{4}{3} I(I+1)H_0^2]}{\Delta H_{EXP}} \quad (79a)$$

$$= \frac{\text{CONSTANT}}{\Delta H_{EXP}} \quad (79b)$$

In view of Equation (75), one sees that a comparison of ω_N and ω_h is similar to a comparison of ΔH_{EXP} and ΔH_{THEORY} .

The data of Morigaki and Mitsuma⁵, presented in Figure 4(b), yields ω_N values as plotted in Figure 11. If hopping were the only mechanism causing the narrowing of the ESR spectrum, ω_N would be equal to ω_h according to the Anderson narrowing theory. But, as stated in Sections II and III and as shown in Equation (61), ω_h approaches zero as T approaches zero. However, in Figure 11 one sees that ω_N does not do so. It appears to approach a constant in the

Figure 11. Plot of ω_N versus T for phosphorus-doped germanium. Equation (79) is used to define ω_N and the seven ΔH_{EXP} data values are from Reference 5 (see Figure 4(b)). Note that ω_N extrapolates to a constant as the temperature approaches zero.

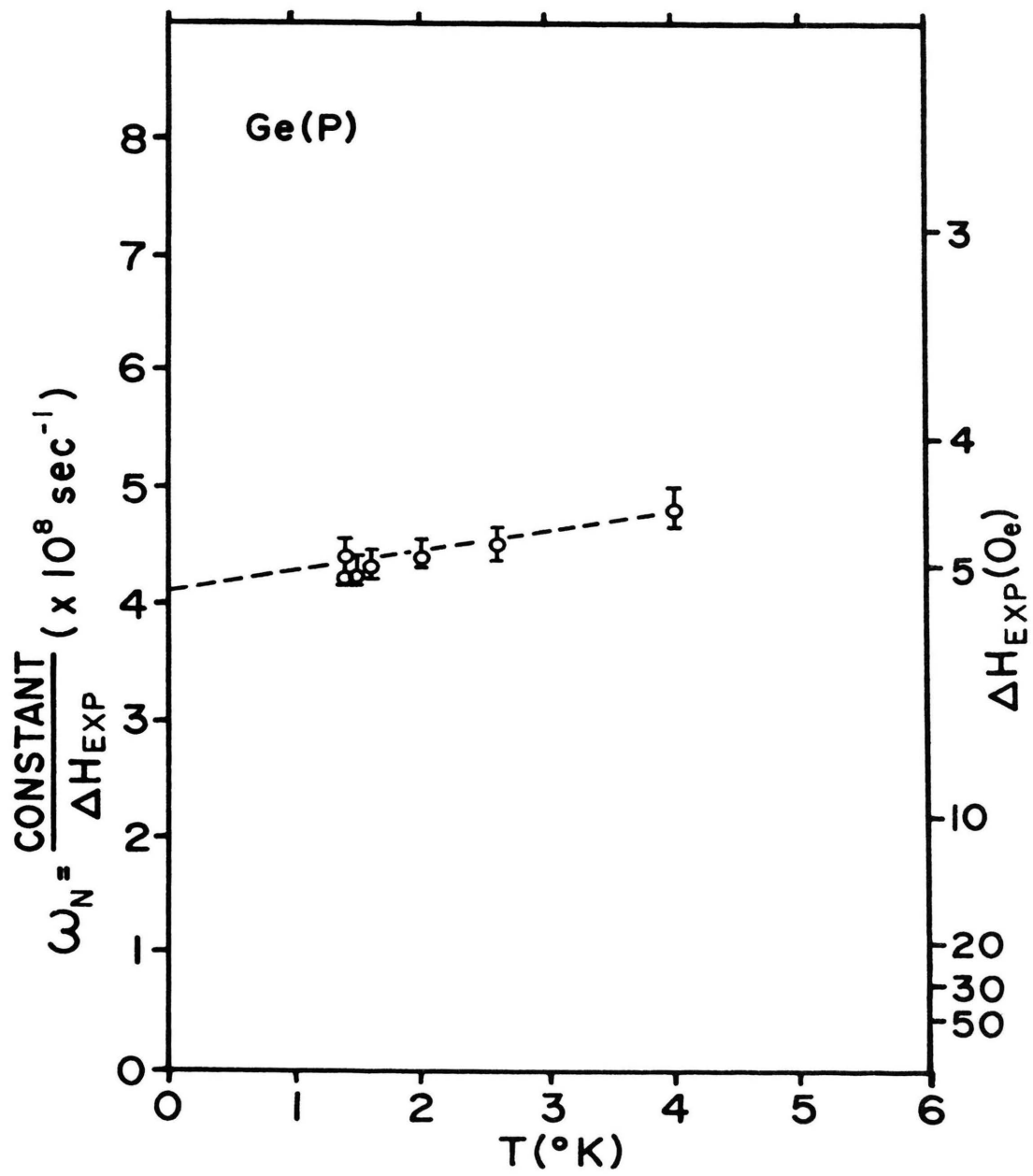


Figure 11

T=0 limit. Hence, narrowing by hopping also does not predict the proper temperature dependence, or at least it does not predict the T=0 intercept. Some other mechanism seems to be contributing to the narrowing.

One might digress for a moment to note here that other authors^{4,10,12,13,23} have treated the problem of narrowing of the donor ESR spectrum, by employing the exchange interaction between donor electrons and the exchange narrowing theory of Anderson and Weiss.¹⁸ However, the treatment of narrowing by most of the former authors involved insertion of parameters such as R_D into previously derived microscopic equations for the exchange interaction from References 17b or 24. The use of this technique of "averaging" has been shown in this thesis to lead to the wrong equations for ω_h . It is far from clear that it is a valid method for averaging the exchange interaction.

If, in the future, the contribution of exchange to the ESR spectral narrowing is to be compared with experiment, or possibly used to explain the T=0 intercept or possibly also the temperature dependence (see Reference 23) of the ω_N versus T curves, the proper method of averaging the exchange interaction over the entire electron and donor ensembles must be used. This technique should include the electron distributions plus an average over donor separations r_{ij} similar to the analytical calculation used in Section III of this thesis or techniques similar to the computer technique used by Cullis and Marko²⁵ to average the temperature independent exchange interaction.

In addition, if the theories of hopping and exchange narrowing are to be applied simultaneously to the case of donor ESR spectra, one must investigate in detail how both these interactions work together to narrow the line. The result of such an investigation might depend upon whether the two narrowing processes are independent, competing, or complementary. It would also depend upon the fact that hopping and the exchange interaction narrow the spectrum in slightly different manners. That is, hopping is a Markhoffian modulation process while exchange is a Gaussian process. (The reader should refer to the Anderson paper¹⁶ for definitions of Markhoffian and Gaussian modulation processes.) Preliminary calculations of Parks²⁶ using the Anderson theory show that if the exchange interaction is much stronger than hopping, that ω_N can be obtained by adding ω_h times a constant to the exchange frequency, $\omega_e = J_e/\hbar$. The constant is of the order of $1/\pi$.

Returning to the discussion at hand, one finds that the most extensive data on donor ESR spectral narrowing in germanium have been taken by Gershenzon, Pevin, and Fogel'son^{12,13} using arsenic-doped samples. Conversion of their data on uncompensated samples from ΔH_{EXP} to ω_N yields curves (see Figure 12) very similar to those of Morigaki and Mitsuma's data for phosphorus-doped germanium. Each curve increases with temperature and each has a T=0 intercept. Note that the difference between ω_N and $\omega_N(T=0)$ for this range of T, N_D , and K is small compared to the value $\omega_N(T=0)$. It thus appears that the greater part of the narrowing is caused by the "T=0 mechanism". Since hopping predicts no T=0 intercept, it can be concluded that

Figure 12. Plot of ω_N versus T for arsenic-doped germanium.

Equation (79) is used to define ω_N and the ΔH_{EXP} data is from Reference 12. Note the factor of ten difference in the ordinate and factor of two difference in the abscissa from Figure 11. The difference in the ordinates is mainly due to the difference in the constant $[\Delta H_0^2 + \frac{4}{3} I(I+1)H_0^2]$ between arsenic and phosphorus donors (see Table II). The various curves are for

- (a) $N_D = 3.4 \times 10^{16} \text{ cm}^{-3}$,
- (b) $N_D = 4.6 \times 10^{16} \text{ cm}^{-3}$,
- (c) $N_D = 7.0 \times 10^{16} \text{ cm}^{-3}$, and
- (d) $N_D = 1.8 \times 10^{17} \text{ cm}^{-3}$.

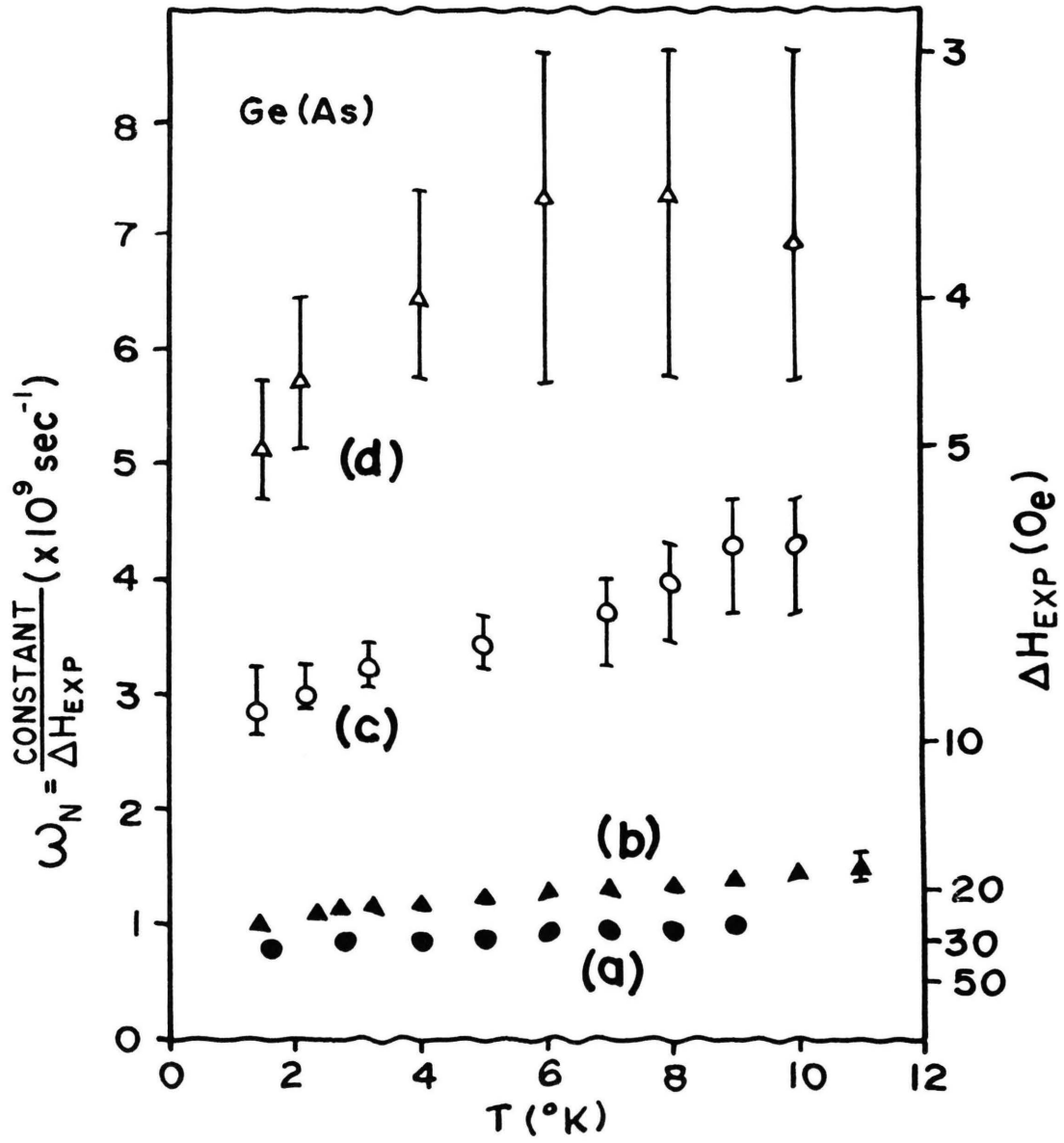


Figure 12

phonon-induced tunneling is not the main contributor to the N_D dependence of ω_N .

Using preliminary results on highly compensated samples in germanium¹³ (and noting similar results in silicon^{27,28}), one might also infer that hopping is not the primary contributor to the narrowing because of the compensation dependence. The experimental results of Gershenzon, et al., show that highly compensated samples exhibit hyperfine structure while uncompensated samples of similar donor concentration exhibit narrowing. Since Equation (61) predicts an increase in ω_h with K , one might tentatively conclude that hopping cannot account for the compensation dependence of the strength of donor ESR line narrowing. However, the data is sparse and, as discussed in the next paragraph, the possibility still remains that hopping could account for the compensation dependence of the slope of the ω_N versus T curves.

None of the conclusions so far has completely ruled out phonon-induced tunneling as a contributing factor in the narrowing of donor ESR spectrum, although they provide strong evidence that it is not the main contributor. It is possible that hopping is causing narrowing over and above what is caused by the mechanism producing the $T=0$ intercept. To test if hopping is providing all the temperature dependence, one may employ the same technique used by Gershenzon, et al., (see Section II). Supposing that the $T=0$ mechanism is temperature independent, one adds its value to the theoretical curves for the hopping frequency and compares the experimental ω_N curves to

$$\omega_h' = \omega_N(T=0) + \omega_h \quad , \quad (80)$$

where ω_h is calculated numerically from Equation (61). Unfortunately, the compensation ratio in Gershenson's, et al., samples was too small to be measured,^{12,13} i.e., below 10^{-2} .

Hence, K can be treated as an adjustable parameter to fit ω_h' to the experimental ω_N curves. The results of the curve fit are shown in Figure 13, and Table III gives the values needed in the fit for the adjustable parameters, $\omega_N(T=0)$ and K (or N_A). While all the K values are below 10^{-2} , they stay constant or even increase as the donor concentration is increased. As discussed earlier in this section, one normally expects the compensation ratio to decrease with increasing N_D for samples not deliberately compensated and grown from the same germanium melt.

The fact that the compensation must increase with N_D to fit the data indicates that hopping would have serious difficulty in explaining the observed narrowing if one made the normal assumption of constant N_A . For example, if $N_A = 7.5 \times 10^{12} \text{ cm}^{-3}$ is chosen for all the samples, then the theoretical curve for ω_h' would fit the experimental data for $N_D = 3.4 \times 10^{16} \text{ cm}^{-3}$. However, as the donor concentration increases, the theoretical curves tend to flatten out while the slope of the experimental data increases. Thus at higher N_D , ω_h' would not fit the data. Similar attempts to choose an N_A from Table III would always yield one curve that fit the data and three others that did not. Thus it appears that if all the samples indeed had the same concentration of acceptors, hopping could not even explain the temperature dependence.

Figure 13. Plot of the fit of ω_h' (solid lines) to the data for ω_N in Figure 12. The parameters used to calculate ω_h' from Equation (80) are listed in Table III. Note that straight lines can fit the data at least as well as the theoretical curves.

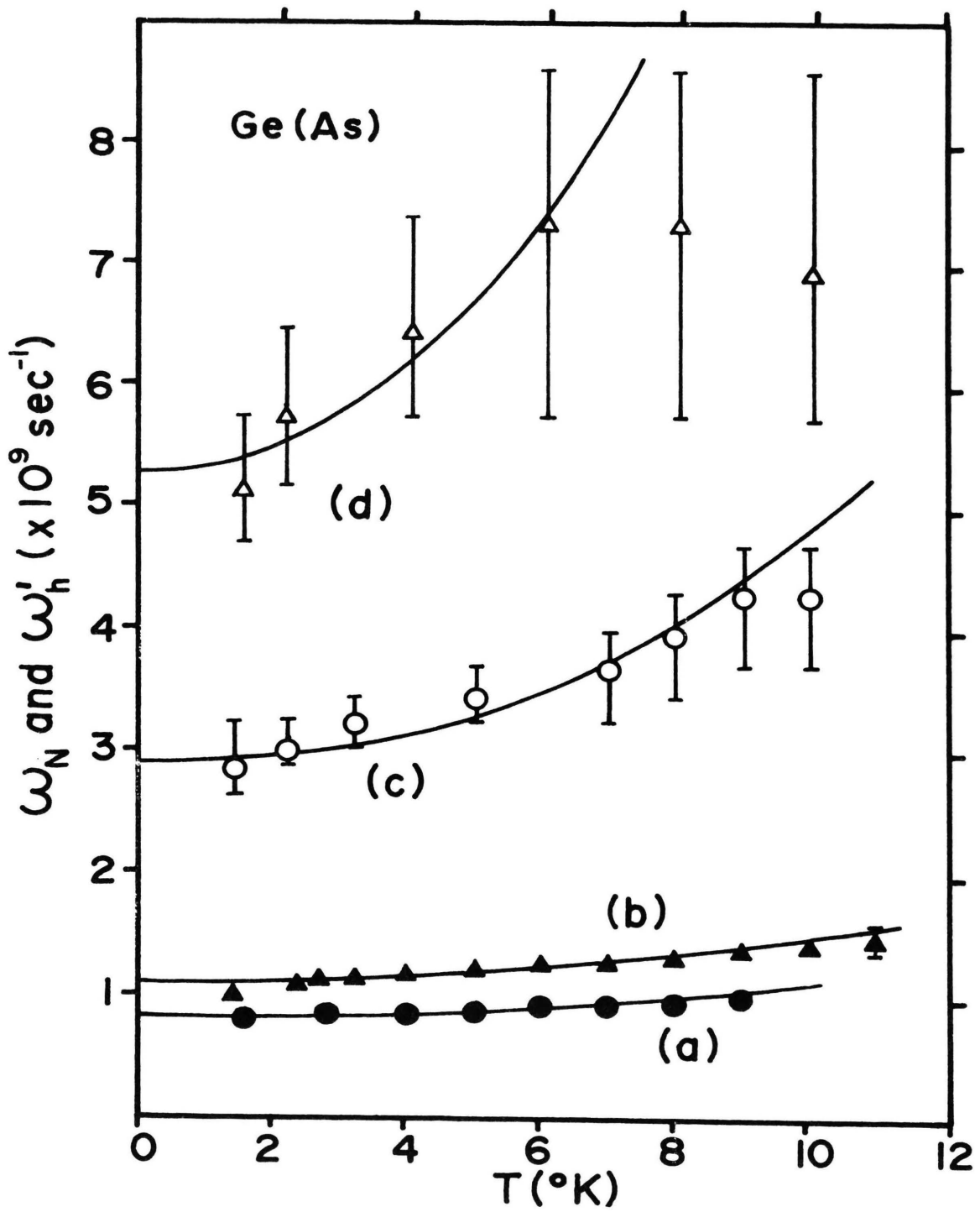


Figure 13

Table III. Values of the adjustable parameters ω_N ($T=0$) and K (or N_A) needed to fit the data points with the curves shown in Figure 13. Note that K must increase with N_D in order to fit, contrary to what one would expect for samples not deliberately compensated.

Table III

N_D (cm^{-3})	ω_N (T=0) (sec^{-1})	K	N_A (cm^{-3})
3.4×10^{16}	8.5×10^8	2.2×10^{-4}	7.5×10^{12}
4.6×10^{16}	1.09×10^9	2.2×10^{-4}	1.0×10^{13}
7.0×10^{16}	2.90×10^9	9.0×10^{-4}	6.3×10^{13}
1.8×10^{17}	5.25×10^9	2.0×10^{-3}	3.6×10^{14}

However, the fact that the theoretical K does not follow what is expected from residual acceptors in the germanium is not conclusive proof that hopping is not causing the temperature dependence of ΔH_{EXP} . The compensation may not be due to substitutional acceptors alone. Other centers, such as dislocations, might also trap electrons and cause an effective compensation ratio.

There is still another reason, though, for casting doubt on the explanation for the T dependence of ΔH_{EXP} by narrowing due to hopping. The ω_N versus T curves are almost linear in temperature. Yet ω_h' versus T rises slowly from $T=0$ and does not exhibit a linear T dependence until the temperature is fairly high (see Figure 8 or 9). However, the error bars on the data in Figure 13 are such that one cannot be certain that ω_N does indeed vary linearly with T . Hence, the possibility still exists that hopping can cause the temperature dependence. This conclusion is contrary to that of Gershenzon, et al.,¹³ who concluded that hopping cannot be causing any of the narrowing of the donor ESR line width.

Having studied ESR line narrowing data in germanium, one might also attempt to quantitatively study similar data in silicon. However, due to the fact that there is about a factor of five discrepancy in the ΔH_{EXP} data on phosphorus-doped silicon between Reference 7 and Reference 9, only a few qualitative statements can be made about donor ESR spectral narrowing in silicon. Figure 14 shows some data taken from Reference 9 on ΔH_{EXP} . The main point to note is the similarity between Figures 4 and 14, even though one plot

Figure 14. Plot of data on ΔH_{EXP} , the line width between the inflection points of the narrowed line, for phosphorus-doped silicon. Data taken from Reference 10.

Plot (a): Donor concentration dependence (i.e., R_D dependence where $R_D = (3/4\pi N_D)^{1/3}$) vs ΔH_{EXP}

Plot (b): Temperature dependence vs ΔH_{EXP} for
curve (1) $N_D = 1.54 \times 10^{18} \text{ cm}^{-3}$; for
curve (2) $N_D = 1.74 \times 10^{18} \text{ cm}^{-3}$; and for
curve (3) $N_D = 1.77 \times 10^{18} \text{ cm}^{-3}$.

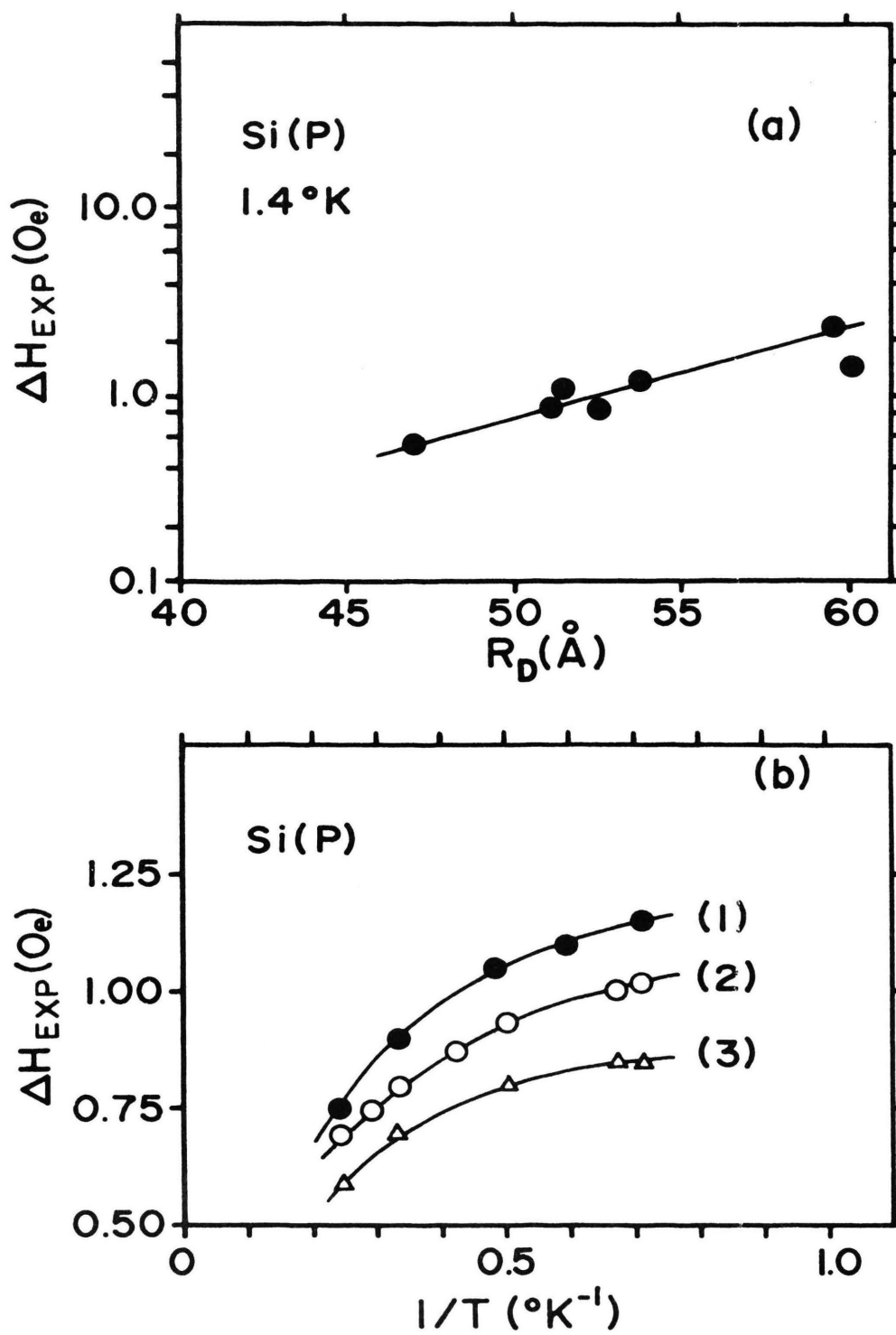


Figure 14

is for germanium and the other is for silicon. However, the concentration range in which these effects occur is much higher in silicon (10^{17} to 10^{18} cm^{-3}) than in germanium (10^{16} to 10^{17} cm^{-3}). This effect has been attributed to the fact that electrons are more tightly bound to donors in silicon.¹² That is, whatever the narrowing mechanism, if it depended upon the interaction of the donor electron wave functions, the concentration at which this mechanism would become significant would be much higher in silicon than in germanium. Except for the concentration differences, donor ESR narrowing appears to be caused by the same mechanism at liquid helium temperatures no matter which Group IV semiconductor is chosen for the host crystal. Additional experiments^{11a,b} in other n-type semiconductors (InSb) indicate that the narrowing of donor ESR spectra is not unique to Group IV semiconductors and can probably be explained with the same mechanisms.¹²

C. A POSSIBLE EXPERIMENT FOR RESOLVING THE PROBLEM OF NARROWING BY HOPPING

There is one experiment which can be performed which should decide whether or not hopping is a factor in the narrowing of the donor ESR spectrum in semiconductors. A set of samples with the same N_D should be grown such that each sample contains a low, but measurable, compensation ratio. Then ESR should be performed upon these samples to determine the temperature dependence of the narrowed donor line and the data should be converted to ω_N versus T plots with Equation (76). Presumably, the $T=0$ intercepts should decrease with

increasing compensation if the preliminary results or higher compensated samples¹³, mentioned earlier, are valid. If the compensation ratio is not too large, then Equation (63) or (64) may be used to predict the K dependence of ω_h . If hopping is responsible for the temperature dependence, then the slopes of the ω_h versus T curves should agree with the predictions, and increase approximately linearly with K. If this is not the case, hopping can be ruled out.

One must be careful to keep the compensation low in the experiment (i.e., $K \ll K_c$), if good comparisons with theory are to be made. If it becomes too high the low K approximation, does not hold and the average transition rate ω_h must be obtained from the complicated expression in Equation (51). It is fairly evident from the K dependent $G(\Delta)$ function and the phonon factor in Equation (51) that ω_h would not be proportional to K for the case of higher K.

VI. SUMMARY OF FINDINGS AND CONCLUSIONS

This thesis, on the effects of phonon-induced tunneling on the ESR spectrum of donor electrons, has discussed the phenomenon in a wide variety of theoretical and experimental contexts. In particular, past work in the area has been reviewed, a new theory for narrowing by hopping has been derived and related to the existing data, and a few possibilities for future research have been proposed. Because of this diversity, this last section summarizes the progression of the work and the major results which can be derived from the discussion.

First of all, it was shown that the narrowing of ESR spectra of donor electrons had been observed experimentally and that a basic theory of how narrowing might be caused had been introduced. It was found that the degree of narrowing of the observed spectrum increased with increasing donor concentration and increasing temperature for concentrations below impurity banding concentrations ($2 \times 10^{17} \text{ cm}^{-3}$ in Ge and $3 \times 10^{18} \text{ cm}^{-3}$ in Si) and for low temperatures (20 °K or below). It subsequently was shown that a possible means for achieving such narrowing was motion of the spin particles partaking in the ESR experiment. As the motion becomes more rapid, a new ESR line appears in the spectrum and becomes increasingly narrow. (A similar process of narrowing caused by the exchange interaction between the spin particles was not of foremost interest in this work. It became necessary to discuss it only when all the experimental results could not be explained by motion due to hopping.) The source

for a quantitative description of this process was the Anderson theory of motional narrowing.¹⁶ His theory yielded an equation [Equation (3)] for the line breadth in terms of the non-narrowed spectrum and the average rate of motion of the electrons, which was valid if the motion was sufficiently rapid.

Next, the mechanism for causing motion of the electrons, phonon-induced tunneling, was introduced in detail. The main theory used to describe this hopping process was the Miller and Abrahams^{17b,c} calculation of the transition rate for a specific pair of occupied and unoccupied donors (the "microscopic" hopping rate) and their mathematical description of the donor electron ensemble and donor and acceptor impurity ensembles. Miller and Abrahams had used the model and methods of this theory to successfully derive the resistivity of a semiconductor containing substitutional impurities. It was assumed that the same model and methods could be used to calculate an average hopping frequency, the essential quantity needed in the Anderson theory to quantitatively describe the line breadth of an ESR spectrum narrowed by hopping motion.

Before performing any calculations, an extensive survey was conducted of previous work which treated ESR spectral narrowing by hopping. It was found that by not taking several effects into account, previous theories of narrowing were, at best, approximate and in many cases incorrect. While expressions in these earlier theories included a form of the Miller and Abrahams microscopic transition rate, none had treated the problem completely by averaging

this hopping rate over the electron and impurity ensembles. In addition, a minor mistake had been made by not calculating the average square spread of the non-narrowed spectrum $\langle H^2 \rangle_{ave}$, a constant needed in the Anderson narrowing theory to describe the theoretical line width. As a result the conclusions these authors derived from a comparison of their approximate theories with their experiments could not be considered valid. Indeed, some authors had concluded that hopping could definitely explain all the data on ESR spectral narrowing at low temperatures and pre-banding concentrations; others had concluded that motional narrowing by hopping could not in any way explain the line width data.

To resolve the situation, it was necessary to calculate in detail the average transition rate, ω_h , and the average square spread of the non-narrowed spectrum. In the calculation of ω_h , an attempt was made to adhere as closely as possible to the methods of Miller and Abrahams. However, since these authors calculated the resistivity, not the average transition rate, first a definition of ω_h commensurate with the concepts of motional narrowing had to be formulated. Then, the electron statistics and the distributions of the impurities were used to arrive at a formal expression for ω_h . (The value of one parameter in this expression, the ground state Fermi energy ζ_g , could not be immediately obtained. It was necessary to devise techniques, based on the Miller and Abrahams method used for the same purpose, to calculate ζ_g for use in the ω_h expression.) Since the formal expression for ω_h , a triple integral with variable limits, was very complex, useful approximations were sought which would be valid for

the ranges of N_D , N_A , and T on which previous data had been taken. The results of the calculation of ω_h and ζ_g are summarized in Table IV. However, before these results were used to analyze the experimental data, it was necessary to calculate the proportionality constant $\langle H^2 \rangle_{\text{ave}}$ needed in Equation (3). The derivation was based on the definition of this quantity extracted from the Anderson theory of motional narrowing and the results have been summarized in Table II.

The expression for the average hopping frequency was then mated with the equation for the line width to arrive at the new narrowing theory for donor ESR spectra. Subsequent analysis showed major differences between the new theory and the previous theories for the line width. These differences are as follows:

1. The donor concentration dependence (R_D dependence) of the line width is, from Equations (3) and (63), at constant K ,

$$\Delta H_{\text{THEORY}} \propto \frac{1}{N_D} \propto R_D^3$$

for fairly high temperatures. This is contrary to the earlier belief that the line width should be proportional to $\exp(2R_D/a)$. The comparison with previous theory is even worse at lower temperatures, where the dependence of the new theory is, from Equations (3) and (64), at constant K ,

$$\Delta H_{\text{THEORY}} \propto E_D R_D^3 \propto R_D^2 .$$

In fact, the R_D^3 dependence at high T is the strongest dependence of ω_h on R_D . No exponential term in R_D/a has been found.

Table IV. A summary of various expressions for ω_h and ζ_g . Listed are their descriptive names, their equation reference, the conditions under which they are valid, and the reference to the inequality in which this condition is expressed.

Table IV
 ω_h

Name	Equation Number	Restrictive Conditions	Inequality Number
Formal Expression	(51) [see also (A-15)]	Miller and Abrahams ^{17b} framework	--
Low K Approximation, valid for all T	(61)	$K \ll K_c$	(59c)
Low K, High T Approximation	(63)	$K \ll K_c,$ $T \gg T_c'$	(59c) (32b)
Low K, Low T Approximation	(64)	$K \ll K_c,$ $T \ll T_c$	(59c) (29b)

 ζ_g

Name	Equation Number	Restrictive Conditions	Inequality Number
Formal Definition	(26)	Miller and Abrahams framework	--
Low T Approximation, valid for all K	(30)	$T \ll T_c$	(29b)
Low T, Low K Approximation	(31)	$T \ll T_c$ $[-\ln(1-K)] \approx K$	(29b) --
High T Approximation	(34)	$T \gg T_c'$	(32b)

2. As the temperature approaches zero, ω_h approaches zero. Thus ΔH_{THEORY} should approach infinity. (That is, the spectrum should revert to its nonnarrowed form in the $T=0$ limit.) This is contrary to the form for the line width used by many to show agreement with experiment. This former expression [Equation (6)] approached a constant in the $T=0$ limit.
3. The theoretical line width has a strong dependence on the compensation. In particular, for low compensations, it is about

$$\Delta H_{\text{THEORY}} \propto \frac{1}{K} \quad .$$

This fact is contrary to previous authors whose formulas for the line width predicted no significant dependence on the compensation.

4. The new theory predicts line widths for a given hopping frequency a little less than one order of magnitude smaller than those predicted by older expressions for the line width. This result is due to the proper calculation of $\langle H^2 \rangle_{\text{ave}}$.

The new expression for ΔH_{THEORY} was then compared with the experimental data on the line widths observed. It was also convenient at times to compare the inverse of ΔH_{THEORY} and the inverse of ΔH_{EXP} . These comparisons produced some interesting results, many in conflict with earlier findings. The conclusions are as follows:

1. Motional narrowing by phonon-induced tunneling is not the only mechanism causing the ESR spectrum of donor electrons to narrow. The observed spectrum remains narrowed as T approaches zero, contrary to the predictions of narrowing by hopping only.
2. Motional narrowing by phonon-induced tunneling is not the dominant mechanism causing narrowing. Apparently the mechanism defined at $T=0$ is. The line width for a given T exhibits donor concentration and compensation dependences not predicted by hopping.
3. However, motional narrowing by hopping cannot yet be totally ruled out as a contributing factor. The possibility still exists that hopping is causing narrowing over and above the " $T=0$ " mechanism. In addition, the uncertainty in the compensation ratio in samples, when K is less than 1%, destroys the hope of using existing data (which is almost all taken in this range of K) to completely decide if hopping is contributing to narrowing or not.

An experiment was proposed which should resolve the uncertainty in whether or not hopping is contributing to narrowing. It is based upon the assumption that hopping is causing the temperature dependence in ΔH_{EXP} and that the " $T=0$ " mechanism is independent of temperature. Since hopping predicts a linear K dependence in ω_h for low K , the slope of the $1/\Delta H_{\text{EXP}}$ versus T curves should reflect this dependence, if hopping is still contributing to the narrowing.

Finally, a conclusion with respect to theoretical techniques was also drawn:

4. Whether or not the ensembles over which a microscopic quantity varies are taken into account can make a significant difference in the final expression used for such a quantity. If the microscopic quantity Q is a function of a certain parameter p which has a certain probability distribution function in the ensemble and if the distribution is not sharply peaked at a particular value of p , it often happens that the mathematical formula for the macroscopic average of Q will bear little resemblance to that of the original microscopic quantity.

One must be aware of this fact when dealing with other narrowing mechanisms which involve interacting donors. Their effects, as with the effects of hopping, must also be averaged over the electron and impurity ensembles.

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VITA

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During the summers of the years 1966 through 1969 Mr. Meier worked as a research assistant to David Apirion, Professor of Microbiology at Washington University, in St. Louis, Missouri, and co-authored a publication on that work. During the summer of the year 1971 he attended an Air Force Reserve Officer Training Corps camp and has since been enrolled in the AFROTC academic program. From September, 1971 to December, 1971 he was a teaching assistant in the UMR Department of Physics. Since January, 1972 he has held a National Defense Education Act Title IV fellowship and has been an assistant in the research endeavors of Edward B. Hale, Assistant Professor of Physics, at UMR.

On July 16, 1971 David Meier married the former Annetta Louise Schoonover. Mr. and Mrs. Meier are expecting a child in August, 1973.

Appendix A

THE TRANSITION RATE FOR THE HOPPING PROCESS

To find the average frequency with which an electron leaves a donor site due to phonon-induced tunneling, the transition rate for this process must be calculated. Using the model presented in Section I.B. (see Figure (3)) Miller and Abrahams^{17b} have performed such a calculation and applied their results to determining the low temperature resistivity of a semiconductor containing donor and acceptor impurities. To calculate the hopping transition rate, they assumed the Kohn and Luttinger^{21,22} effective mass theory to describe the isolated donor states. They then allowed i and j to interact through a Hamiltonian involving one electron, positively charged centers i and j , and a negatively ionized acceptor. States in which the electron could be localized on i or j were then found by performing a variational calculation on the above Hamiltonian with a linear combination of the Kohn and Luttinger wave functions for i and j . Finally the transition rate was found from the matrix element of the electron-phonon interaction between these two localized states. The mathematics and the results of these steps will be briefly reviewed in this appendix.

The unperturbed wave functions on a donor are given by the effective mass theory of Kohn and Luttinger^{21,22}

$$\psi_i(\vec{R}) = \sum_{p=1}^n \alpha_p F_p(\vec{R}) \phi_p(\vec{R}) \quad , \quad (\text{A-1})$$

where $\phi_p(\vec{R})$ is the Bloch function for the p^{th} conduction band minimum. The $F_p(\vec{R})$ are the hydrogen-like functions

$$F_p(\vec{R}) = (\pi a^2 b)^{-1/2} \exp\{-[(X^2+Y^2)/a^2 + Z^2/b^2]\} \quad . \quad (\text{A-2})$$

Here Z is in the direction of the p^{th} minimum and a and b are the transverse and longitudinal radii of the orbit. The α_p determine the various linear combinations of the $F_p \phi_p$ products that are eigenfunctions of the total Hamiltonian (including the crystal field). In the Si and Ge ground states $\alpha_p = 1/n^{1/2}$ where n is the number of conduction band minima.

Now if i and j are two nearby donors, i neutral and j ionized, and are in the presence of an ionized acceptor, then the Hamiltonian for the donor electron is

$$H = T + V_a - \frac{e^2}{k_0 R_i} - \frac{e^2}{k_0 R_j} \quad . \quad (\text{A-3})$$

T is the kinetic energy operator, V_a is the acceptor potential, $e^2/k_0 R_i(j)$ is the potential due to the donor nucleus at $i(j)$, and k_0 is the dielectric constant of the semiconductor. To find the wave functions which diagonalize this Hamiltonian a variational calculation is done using the trial functions

$$\begin{aligned} \Psi_i &= a_i \psi_i + a_j \psi_j \\ \Psi_j &= \frac{(a_i + a_j S_{ij}) \psi_j - (a_j + a_i S_{ij}) \psi_i}{\sqrt{1 - S_{ij}^2}} \quad , \quad (\text{A-4}) \end{aligned}$$

where

$$S_{ij} = \langle \psi_i | \psi_j \rangle \quad .$$

These constitute an orthonormal set. The variational calculation yields^{17b}

$$\begin{aligned}\Psi_i &\approx \psi_i + \frac{W_{ij}}{\Delta_{ij}} \psi_j \\ \Psi_j &\approx \psi_j - \frac{W_{ij}}{\Delta_{ij}} \psi_i \quad ,\end{aligned}\tag{A-5}$$

where

$$\begin{aligned}W_{ij} &\approx L_{ij}^i - S_{ij} J_{ii}^j \\ \Delta_{ij} &= E_i - E_j \\ L_{ij}^i &= -\langle \psi_i | \frac{e^2}{k_0 R_i} | \psi_j \rangle \\ J_{ii}^j &= -\langle \psi_i | \frac{e^2}{k_0 R_j} | \psi_i \rangle \\ E_i &= \langle \psi_i | V_a | \psi_i \rangle \quad .\end{aligned}\tag{A-6}$$

Equation (A-5) is valid only if $W_{ij} \ll \Delta_{ij}$. Often W_{ij} is called the resonance energy and is the "overlap energy" referred to in Section I.B. The quantity E_i is the energy perturbation due to the acceptor. Its value for the ground state is approximately the value of the coulomb potential of that acceptor at site i ^{17b}

$$E_i \approx \frac{e^2}{k_0 r_{iA}}\tag{A-7}$$

if the unperturbed ground state is taken to be $E=0$. As is seen above, the energy difference between sites Δ_{ij} must be much larger than the resonance energy to have localized states on i and j .

To find the hopping transition rate, the matrix element of the electron-phonon interaction is needed. In the deformation potential approximation the electron-phonon perturbation for absorption ($\Delta_{ij}<0$) is^{17b}

$$H' = E_1 \sum_k \left(\frac{\hbar k}{2\rho_0 V c} \right)^{\frac{1}{2}} e^{i\vec{k}\cdot\vec{R}} (a_k - a_{-k}^\dagger) \quad (A-8)$$

and

$$\langle \Psi_j | H' | \Psi_i \rangle = i E_1 \sum_k \left(\frac{\hbar k n_k}{2\rho_0 V c} \right)^{\frac{1}{2}} \frac{W_{ij}}{\Delta_{ij}} (e^{i\vec{k}\cdot\vec{r}_{ij}} - 1) \quad (A-9)$$

where n_k is the number of phonons in the k state; ρ_0 , V , and c are the density, volume, and speed of sound of the crystal;

$\vec{r}_{ij} = (x_{ij}, y_{ij}, z_{ij})$ is the vector separating i and j ; and E_1 is the relevant deformation potential constant. Using the "Fermi golden rule", Miller and Abrahams^{17b} arrived at the following expression for the transition rate for absorption

$$U_{ij}^{(ab)} = \left(\frac{E_1^2}{\pi \rho_0 c^5 \hbar^4} \right) W_{ij}^2 |\Delta_{ij}| \frac{1}{e^{\beta|\Delta_{ij}|} - 1} \quad (A-10)$$

Since $|\Delta_{ij}|$ is the phonon energy, $(\exp(\beta|\Delta_{ij}|) - 1)^{-1}$ has been substituted for n_{k_Δ} where k_Δ is the magnitude of the wave vector of the phonon with energy Δ_{ij} . For emission ($\Delta_{ij}>0$) the resulting transition rate is^{17b}

$$U_{ij}^{(em)} = \left(\frac{E_1^2}{\pi \rho_0 c^5 \hbar^4} \right) W_{ij}^2 \frac{\Delta_{ij}}{1 - e^{-\beta \Delta_{ij}}} . \quad (A-11)$$

The remaining quantity to be determined is W_{ij}^2 . Using Equations (A-1), (A-2), and (A-6), Miller and Abrahams find that

$$|W_{ij}|^2 = \left(\frac{2e^2}{3nk_0 a^2} \right)^2 \sum_{p=1}^n r_p^2 \exp(-2r_p/a) , \quad (A-12)$$

where $r_p = a((x_{ij}^2 + y_{ij}^2)/a^2 + z_{ij}^2/b^2)^{1/2}$. If the effective mass is very anisotropic then an angular average over the conduction band minima can be computed

$$\langle |W_{ij}|^2 \rangle = \left(\frac{2e^2}{3k_0 a^2} \right) \left(\frac{1}{n} \right) \left\{ \frac{\pi a}{4[(a^2/b^2) - 1] r_{ij}} \right\}^{1/2} r_{ij}^2 \exp(-2r_{ij}/a) . \quad (A-13)$$

If the mass is isotropic, then the quantity in braces is replaced by unity.

Summarizing, then, the transition rate between the ground state on i to the ground state on j , regardless of the sign of Δ_{ij} , is

$$U_{ij} = \frac{1}{B} r_{ij}^{3/2} \exp(-2r_{ij}/a) \frac{\Delta_{ij}}{1 - \exp(-\beta \Delta_{ij})} , \quad (A-14)$$

where

$$\frac{1}{B} = \left(\frac{E_1^2}{\pi \rho_0 c^5 \hbar^4} \right) \left(\frac{2e^2}{3k_0 a^2} \right) \left(\frac{1}{n} \right) \left\{ \frac{\pi a}{4[(a^2/b^2) - 1]} \right\}^{1/2} . \quad (A-15)$$

Table A-I gives all the pertinent constants used in the calculation of $1/B$ for various host crystals and doping elements.

In summary, U_{ij} is the transition rate for a hopping electron, given that i is occupied and j is not, that i and j are separated by a distance r_{ij} , and that their ground state energies differ by an energy Δ_{ij} . To find the average transition rate, distributions of electrons on donors and distributions of r_{ij} and Δ_{ij} must be taken into account.

Table A-I. Transverse and longitudinal radii (a and b, respectively) for some donor ground states in germanium (a) and silicon (b). Values for the deformation potential constant, density, speed of sound, dielectric constant, and number of conduction band minima are also given.

Table A-I

(a) Germanium¹⁵
 $E_1=11.4$ eV $\rho_0=5.32$ g/cm³ $c=3.83 \times 10^5$ cm/sec $k_0=16.1$ $n=4$

Doping Element	a (Å)	b (Å)
As	60.5	13.6
Sb	69.5	15.6

(b) Silicon¹⁵
 $E_1=6.25$ eV $\rho_0=2.33$ g/cm³ $c=6.60 \times 10^5$ cm/sec $k_0=11.2$ $n=6$

Doping Element	a (Å)	b (Å)
As	20.2	8.9
P	21.2	9.3
Sb	22.6	9.9

Appendix B

HOPPING APPLIED TO THE ANDERSON NARROWING THEORY

Since the Anderson¹⁶ model of motional narrowing is to be used and since it was not derived precisely for the case of phonon-induced tunneling, it is of interest to determine if hopping can narrow the donor ESR spectrum in the manner described by Anderson. In this appendix it is shown that the relationships between phonon-induced tunneling of donor electrons and the ESR spectrum of donor electrons required by Anderson for application of his theory exist and therefore that hopping is a narrowing process. Without rederivation, the results of the Anderson narrowing theory pertinent to the present problem are then presented and discussed.

If H_0 is the unperturbed Zeeman Hamiltonian, H_p is the hyperfine splitting term, H_m is the motional Hamiltonian, and if $H = H_0 + H_p + H_m$ is the spin Hamiltonian of the donor electron, then three assumptions must be verified in order to apply the Anderson model:

$$[\hat{H}_m, \hat{H}_0] = 0 \quad , \quad (B-1)$$

$$[\hat{H}_m, \mu] = 0 \quad , \quad (B-2)$$

where μ = radiation dipole moment,

$$i\hbar \frac{\partial \hat{H}_p}{\partial t} = [\hat{H}, \hat{H}_p] = [\hat{H}_0, \hat{H}_p] + [\hat{H}_m, \hat{H}_p] \quad ,$$

that is,

$$[\hat{H}_m, \hat{H}_p] \neq 0 \quad . \quad (B-3)$$

The first two assumptions (B-1) and (B-2) are that the motion can change neither the Zeeman interaction nor the radiation involved in the ESR experiment. Assumption (B-3) is equivalent to saying that hopping causes motion between the hyperfine spin states of the donor electron. That is, electron motion between donors can change the hyperfine interaction term of the electron.

The "unperturbed" Hamiltonian can be written as

$$\hat{H}_0 = - \sum_{i\alpha} g \mu_B \vec{s}_{i\alpha} \cdot \vec{H} \quad , \quad (B-4)$$

where the magnetic field is taken in the [100] or z direction. The subscripts i and α denote the donor and the electronic state in which the electron is localized. The hyperfine structure terms contain the Fermi contact term at the donor nucleus plus the Fermi contact term at the surrounding semiconductor nuclei:

$$\hat{H}_p = A \sum_{i\alpha} \vec{s}_{i\alpha} \cdot \vec{I}_i |\psi_{i\alpha}(0)|^2 + A \sum_{i\alpha} \vec{s}_{i\alpha} \cdot \sum_{\ell} \vec{I}_{\ell} |\psi_{i\alpha}(\vec{r}_{\ell})|^2 \quad . \quad (B-5)$$

Here \vec{I}_i is the spin of the donor nucleus i while \vec{I}_{ℓ} is the spin of one of the surrounding semiconductor nuclei and A is the Fermi contact constant. The factor $|\psi_{i\alpha}(0)|^2$ is non-zero only for S states.⁴ Hence when considering the hyperfine spectrum and how it narrows at low temperatures one need consider only the ground state electrons. This is done in the text (see Section III). Finally the motional Hamiltonian is the electron-phonon interaction:

$$\hat{H}_m = E_1 \sum_i \sum_k \left(\frac{\hbar k}{2\rho_0 V c} \right)^{\frac{1}{2}} e^{i\vec{k} \cdot \vec{R}_i} (a_k - a_{-k}^\dagger) \quad , \quad (B-6)$$

\vec{R}_i is the position of the i^{th} donor electron. This expression is equivalent to the Hamiltonian in Equation (A-8).

Since the electron-phonon interaction does not couple with the spin of the tunneling electron, one readily sees that the spacial H_m commutes with the spin H_0 . Thus Equation (B-1) is satisfied. Likewise H_m commutes with the radiation dipole moment, the [010] or [011] component of the electron spin, and thus satisfies Equation (B-2). However the nuclear spin vectors \vec{I}_i and \vec{I}_ℓ are randomly distributed over the donors and semiconductor nuclei in their respective quantum states. Hence the nuclear spin vectors vary from donor to donor, causing the H_p term to have a spacial dependence. In general, then, H_m and H_p do not commute. Thus, Equations (B-1) through (B-3) have been satisfied.

The final condition that must be met is that the average probability ω_h of hopping to a particular spin state (to a particular frequency, in Anderson terminology) in the spectrum is independent of the state in which the electron may have been previously. This is easily seen to be the case with hopping, since the vectors I_i and I_ℓ are randomly oriented, independent of any other nuclear spin vectors. Thus the particular hyperfine interaction which results after a hop depends only upon the donor on which the electron finally becomes localized.

With the above conditions, the results of the Anderson narrowing theory can be applied to the ESR spectrum in the presence of hopping. Accordingly, a single line of breadth (half-width at half-max) $\Delta\omega$ will be observed if the hopping is rapid enough, i.e., if $\omega_h \gg \Delta\omega$. Then $\Delta\omega$ is given by¹⁶

$$\Delta\omega = \frac{\langle \omega^2 \rangle_{\text{ave}}}{\omega_h} . \quad (\text{B-7})$$

With Equation (B-7) the rapid motion condition is

$$\omega_h \gg [\langle \omega^2 \rangle_{\text{ave}}]^{1/2} . \quad (\text{B-8})$$

The quantity $\langle \omega^2 \rangle_{\text{ave}}$ is the mean square breadth of the non-narrowed spectrum and is found by integrating the expression

$$\langle \omega^2 \rangle_{\text{ave}} = \int_{-\infty}^{\infty} \omega^2 P(\omega) d\omega , \quad (\text{B-9})$$

where $P(\omega)$ is a normalized distribution describing the shape of the non-narrowed spectrum and has been shifted along the frequency axis so that its center is at $\omega=0$.

Since the frequency spectrum and magnetic field spectrum are related by

$$\hbar\omega = g \mu_B H , \quad (\text{B-10})$$

where μ_B is the Bohr magneton and g is the Landé g -factor, the above equations may be expressed in terms of the magnetic field. The result is that the narrowed line breadth is

$$\Delta H = \frac{g \mu_B \langle H^2 \rangle_{\text{ave}}}{\hbar \omega_h} \quad (\text{B-11})$$

and the rapid motion condition is that

$$\omega_h \gg \frac{g \mu_B [\langle H^2 \rangle_{\text{ave}}]^{1/2}}{\hbar} \quad , \quad (\text{B-12})$$

where $\langle H^2 \rangle_{\text{ave}}$ is defined in a manner similar to that of $\langle \omega^2 \rangle_{\text{ave}}$ with a corresponding $P(H)$ which describes the non-narrowed magnetic field spectrum. Expression (B-11) determines the breadth of the narrowed line. Theoretically one calculates the two quantities ω_h and $\langle H^2 \rangle_{\text{ave}}$ and compares ΔH with the observed line breadth.

Appendix C

COMPUTER METHODS USED IN CALCULATING ζ_g AND ω_h

Some attention should be given to the numerical methods of solving Equation (26) for ζ_g or for integrating Equation (61). In Equation (26) the equation for the Fermi energy is

$$K = \int_0^{\infty} \frac{F(E) dE}{[1 + e^{-\beta(E-\zeta_g)}]} \quad , \quad (C-1)$$

where K , E_A , and $\beta=1/k_B T$ are given. A convenient method of solving a transcendental equation of this sort is by a variation of Newton's approximation method. If ζ_g' is the new approximation to ζ_g and ζ_{g0} is the first approximation then

$$\zeta_g' = \zeta_{g0} + \frac{d\zeta_g}{dK} (K - K_0) \quad , \quad (C-2)$$

where K_0 is the value obtained from Equation (C-1) if ζ_{g0} is used in the integration. Now

$$\frac{d\zeta_g}{dK} = \frac{1}{dK/d\zeta_g} = - \left\{ \int_0^{\infty} \frac{F(E) \beta dE}{[1 + e^{-\beta(E-\zeta_g)}] [1 + e^{\beta(E-\zeta_g)}]} \right\}^{-1} \quad . \quad (C-3)$$

Hence integrating Equations (C-1) and (C-3) and iterating on Equation (C-2) until $|K - K_0|$ is small enough will yield ζ_g . A convenient first approximation is $\zeta_{g0} = E_A / (-\ln(1-K))^{1/3}$, the $T=0$ Fermi energy.

The integration process is very important since very accurate integrals must be performed quickly. The method most suited to integrating from zero to infinity rapidly is to split the integral into two parts and change variables on one:

$$\int_0^{\infty} \frac{F(E) dE}{[1+e^{-\beta(E-\zeta_g)}]} = \int_0^{\zeta_{go}} \frac{F(E) dE}{[1+e^{-\beta(E-\zeta_g)}]} + \int_{\zeta_{go}}^{\infty} \frac{3E_A^3}{E^4} \frac{e^{-(E_A/E)^3} dE}{[1+e^{-\beta(E-\zeta_g)}]}$$

$$= \int_0^{\zeta_{go}} \frac{F(E) dE}{[1+e^{-\beta(E-\zeta_g)}]} + \int_0^{(\frac{E_A}{\zeta_{go}})^{\frac{1}{3}}} \frac{e^{-x} dx}{[1+e^{-\beta(E_A/x^{\frac{1}{3}}-\zeta_g)}]} \quad (C-4)$$

These integrals over finite intervals can then easily be performed using ten-point Gaussian quadrature on small subintervals of $(0, \zeta_{go})$ and of $(0, (E_A/\zeta_{go})^{1/3})$, doubling the number of subintervals until a desired accuracy is achieved. A typical integration time is between ten and twenty seconds on a HP 2114 minicomputer, yielding a calculation time for ζ_g of about one or two minutes. Note that after the iteration process the final value obtained from Equation (C-3) can be substituted into Equation (61) for calculation of the averaged transition rate ω_h .