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Evaluation of a model for the contribution of phonon-induced tunneling to donor ESR spectral narrowing in germanium*

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The model commonly assumed to explain the narrowing of the ESR spectra of donor impurities in germanium is examined in detail. This model combines the Anderson line-narrowing theory with the Miller and Abrahams theory for the phonon-induced tunneling (hopping) of an electron between impurities. The predictions of this model are found to be in drastic disagreement with experimental results now available. It is shown that the narrowed linewidth should depend strongly on donor concentration, acceptor concentration, and temperature. Future spin-resonance experiments in highly compensated samples may show the effects of hopping, but no evidence now exists which indicates that hopping is influencing the narrowing of the ESR spectra.

I. INTRODUCTION

It has been well established that shallow-donor electron-spin-resonance spectra in semiconductors become narrower with increasing donor concentration and temperature.¹⁻²⁵ To explain the observed narrowed linewidth, the narrowing equation of Anderson^{26,27}

$$\Delta H = \frac{g\mu_B \langle H^2 \rangle_{av}}{\hbar\omega}, \quad (1.1)$$

has often been used. Where ΔH is the line breadth (equal to one-half the linewidth at half-maximum), $\langle H^2 \rangle_{av}$ is the mean-square spread of the non-narrowed spectrum from its center, and, for motional narrowing, ω is the averaged transition rate between hyperfine states.

This paper considers in detail the motional narrowing which would result from the so-called "hopping" mechanism. This mechanism is the phonon-assisted tunneling of an electron from an occupied donor to an unoccupied donor. In this process, the hyperfine state changes because the electron moves to a different donor nucleus. If the average hopping transition rate, ω_h , is sufficiently fast, the observed spectrum will be narrowed to a single line, whose breadth is given by Eq. (1.1) with $\omega = \omega_h$.

The narrowed donor spectrum in germanium was first observed in 1959 and was attributed to motional narrowing.⁷ It was later proposed that the hopping model of Miller and Abrahams²⁸ described this motion.¹ Linewidth data in various semiconductors has subsequently been analyzed^{1,2,5,11-13,16,29} using Eq. (1.1) and various forms for ω_h which were nonrigorously adapted from the hopping model. The purpose of this paper is to clarify how hopping will influence the spectra. In particular, the theoretical linewidth is determined as a function of the system parameters, such as tempera-

ture, donor concentration, and acceptor concentration. This is done by computing ω_h using the appropriate rigorous expression derived within the framework of the Miller and Abrahams model. This derivation is carried out in Sec. II. In Sec. III the calculations are compared with the data. Discussion and conclusions are presented in Sec. IV. This research was motivated by the considerable confusion, which has existed for about ten years, over how the ESR spectrum would be influenced by the hopping motion. As will be shown, it appears that the effects of hopping on the spectra have not been observed.

II. CALCULATION OF THE AVERAGE HOPPING TRANSITION RATE

A. The model

In the Miller and Abrahams model²⁸ the crystal is a group-IV semiconductor with dielectric constant κ_0 . It is doped with a random distribution of N_D donors and N_A acceptors. 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 at low temperature. The ground state of a given donor is perturbed by the electric field of the nearest negatively charged acceptor. If the unperturbed ground-state energy is taken as $E = 0$, then the ground-state energy of the i th donor is $E_i = e^2/(\kappa_0 r_{iA})$, where r_{iA} is the distance from donor i to the nearest acceptor.

If the donor concentration is sufficiently high, an occupied donor i and an unoccupied donor j may interact because of the overlap of their wave functions. They would form a hydrogeniclike molecular ion except for the perturbation due to the nearest acceptor, which tends to localize the electron on the lower-energy donor site. A change of state involves a phonon with energy $\Delta_{ij} = E_i - E_j$, and the

transition of an electron from donor site i to donor site j .

To determine the breadth of the motionally narrowed line from Eq. (1.1), the average transition rate for an electron, $\omega_h = \omega$, must be determined. If U_i is the electron transition rate from donor i , then ω_h may be obtained by averaging U_i over the electron ensemble. In essence, this is an average over the occupied donors and thus,

$$\omega_h = \sum_{i=1}^{N_D} f_i^0 U_i / \sum_{i=1}^{N_D} f_i^0, \quad (2.1)$$

where f_i^α is the probability that the state α on donor i is occupied by an electron. The average is performed only over the ground state, i.e., $\alpha = 0$, because we are only concerned with narrowing of the ground-state hyperfine interactions. (In the temperature range of interest, most of the electrons are in their ground state and there are few phonons available to produce hopping into excited states.)

The total transition rate from i is a sum over all the transition rates to the various final states on the vacant donors. That is,

$$U_i = \sum_{j=1}^{N_D} \left(1 - \sum_{\delta} f_j^\delta\right) U_{ij} = \sum_{j=1}^{N_D} W_{ij}, \quad (2.2)$$

where U_{ij} is the transition rate from i to j if i is occupied and j is not and W_{ij} is defined by the equation.

The transition rate between donors for phonon-induced tunneling has previously been calculated to be²⁸

$$U_{ij} = \frac{1}{B} r_{ij}^{3/2} e^{-2r_{ij}/a} \left(\frac{\Delta_{ij}}{1 - e^{-\beta \Delta_{ij}}} \right), \quad (2.3)$$

where

$$\frac{1}{B} = \frac{E_1^2}{\pi \rho_0 c^5 \hbar^4} \left(\frac{2e^2}{3k_0 a^2} \right) \frac{1}{n} \left(\frac{\pi a}{4[a^2/b^2 - 1]} \right)^{1/2}. \quad (2.4)$$

Here, ρ_0 and c are the density and speed of sound in the crystal, E_1 is the relevant deformation-potential constant, a and b are the transverse and longitudinal radii of the donor wave function, and r_{ij} is the distance separating donors i and j . (In the past ω_h has often been taken to be U_{ij} with r_{ij} set equal to the average donor separation and Δ_{ij} presumably determined by fitting to a few data points.)

B. Electron statistics

The distribution of electrons and vacancies on donors is embodied in the f_i^α function. By considering the detailed balance equation, Miller³⁰ found

that

$$f_i^\alpha = \frac{\exp[-\beta(E_i^\alpha - \zeta)]}{1 + \sum_{\delta} \exp[-\beta(E_i^\delta - \zeta_g)]}, \quad (2.5)$$

where E_i^α is the energy of the electron in the α state on donor i . The Fermi energy ζ_g is obtained in Appendix A in the case where the temperature is sufficiently low so that the excited donor states are unoccupied.

C. Distribution of the impurities

One may convert the summations in Eqs. (2.1) and (2.2) to integrals by assuming a random geometrical distribution for the donors. Consider a coordinate system with the origin at the donor i and with z axis along the \hat{r}_{iA} direction. Then Eq. (2.2) becomes

$$U_i = U(E_i) = 4\pi N_D \int_0^\infty dr \int_{\Delta^-}^{\Delta^+} d\Delta r^2 G(\Delta) W(E_i, r, \Delta), \quad (2.6)$$

where the integration over ϕ has been performed and the θ integration has been changed to one over Δ by use of the normalized distribution function $G(\Delta)$ with limits Δ^- and Δ^+ (see Appendix B).

To evaluate the sum over i in Eq. (2.1) it is convenient to sum the donors according to their various ground-state energies E_i and to introduce a density of states $F(E_i)$. If a Poisson distribution for the separation r_{iA} of a donor and its nearest acceptor is assumed, then $F(E_i)$ has the form²⁸

$$F(E_i) = \frac{3E_A^3}{E_i^4} e^{-(E_A/E_i)^3}, \quad (2.7)$$

where $E_A = e^2/\kappa_0 R_A$ and $R_A = (3/4\pi N_A)^{1/3}$.

D. Formal expression for the average hopping transition rate

Combining Eqs. (2.1) through (2.3)–(2.7), (B3), and (B4), one obtains

$$\omega_h = \frac{12\pi N_D}{B(1-K)} \int_0^\infty dE \frac{E^3}{E^4} \frac{e^{-(E_A/E)^3} [I_1(E) + I_2(E)]}{1 + e^{\beta(E - \zeta_g)}}, \quad (2.8)$$

where

$$I_1(E) = \int_0^{e^2/\kappa_0 E} \int_{\Delta^-}^{\Delta^+} \frac{\Delta G(\Delta) r^{7/2} e^{-2r/a}}{(1 - e^{-\beta \Delta}) [1 + e^{-\beta(E - \Delta - \zeta_g)}]} d\Delta dr, \quad (2.9)$$

$$I_2(E) = \int_{e^2/\kappa_0 E}^\infty \int_{\Delta^-}^{\Delta^+} \frac{\Delta G(\Delta) r^{7/2} e^{-2r/a}}{(1 - e^{-\beta \Delta}) (1 + e^{-\beta(E - \Delta - \zeta_g)})} d\Delta dr, \quad (2.10)$$

with

$$\Delta_1^+ = \Delta_2^+ = \frac{Er}{(e^2/\kappa_0 E + r)}, \quad \Delta_1^- = \frac{-Er}{(e^2/\kappa_0 E - r)},$$

and

$$\Delta_2^- = \frac{-E(2e^2/\kappa_0 E - r)}{(r - e^2/\kappa_0 E)}.$$

Equation (2.8) represents the formal expression for the average transition rate obtained by considering ground-state hopping in the Miller and Abrahams model.

Equation (2.8) may be solved by various approximations or by numerical techniques. Since most of the data has been taken in the low-compensation region,¹⁻²⁰ a low- K approximation of this equation is developed below.

E. Low-compensation approximation for the average hopping transition rate

1. Low- K approximation valid for all temperatures

Consider the integrations over r and Δ in Eq. (2.8). It can be shown that the integral $I_1(E)$ dominates.³¹ When the length of the interval $(\Delta_1^+ - \Delta_1^-)$ is smaller than $k_B T$, then the $\Delta/(1 - e^{-\beta\Delta})$ function is slowly varying in the range $\Delta_1^- < \Delta < \Delta_1^+$ and is approximately $k_B T$. The criterion for $(\Delta^+ - \Delta^-) \ll k_B T$ is³¹

$$K \ll \frac{R_D}{63.6a} \equiv K_c. \quad (2.11)$$

With this low- K approximation, one obtains by integrating over Δ and r

$$\omega_h = D \frac{N_D}{(1-K)} k_B T \int_0^\infty dE \times \frac{3E^3 e^{(-EA/E)^2}}{E^4 (1 + e^{\beta(E-\zeta_g)})(1 + e^{-\beta(E-\zeta_g)})}, \quad (2.12)$$

where $D = 4\pi (a/2)^{9/2} \Gamma(9/2)/B$. (A small term inside the integral proportional to $\Gamma(9/2, e^2/\kappa_0 aE)$ $\Gamma(9/2)$ has been dropped.) Analytical approximations to solve Eq. (2.12) are presented below. (Numerical solutions of Eq. (2.12) do indeed justify the use of these approximations.³¹)

2. Low-temperature and high-temperature approximations for low- K

For low T , the product of the electron distribution functions in the integrand of Eq. (2.12) is sharply peaked at $E = \zeta_g$. Thus, evaluating $F(E)$ at ζ_g , integrating over E , and inserting the low temperature ζ_g given by Eq. (A2) yields

$$\omega_h = 3DN_A \frac{(k_B T)^2}{E_D}, \quad (2.13)$$

which is valid if³¹ $T \ll T_c \equiv E_A / \{10.6 k_B [-\ln(1-K)]^{4/3}\}$.

For high temperatures, the product of the two-electron distribution functions may be considered slowly varying when $T \gg T'_c \approx 0.66 E_A / k_B$. Then, $F(E)$ is sharply peaked at $E_0 = (3/4)^{1/3} E_A$, and the other function of E can be removed from the integral and evaluated at $E = E_0$. If the high temperature ζ_g from Eq. (A5) is used, the result is

$$\omega_h = DN_A (k_B T). \quad (2.14)$$

Note that the temperature is high in the sense that the product distribution is not sharply peaked at $E = \zeta_g$. However, it is low in the sense that most electrons are still in the donor ground states.

F. Physical interpretation of results

For low compensation, ω_h depends on temperature and impurity concentrations as given in the important Eqs. (2.13) and (2.14). A review of the derivation of these equations shows that the N_D , N_A , and T dependences were primarily determined by three features discussed below.

The phonon involvement [term in large parenthesis in Eq. (2.3)], along with the transition matrix element, leads to a linear temperature dependence, i.e., a $k_B T$ factor, in both the low- and high-temperature cases. This occurs because the integration over the impurity distribution function [Eq. (2.7)] restricts the vacant donor to be near the occupied donor and far from the acceptor when the compensation is low, i.e., the integral I_2 can be neglected in Eq. (2.8). In the I_1 integration, a "high-temperature" phonon approximation is valid and yields a $k_B T$ factor.

In the low-temperature approximation, the transition rate is limited by the number of available initial states since only those electrons in an energy interval of $k_B T$ at the Fermi energy can hop. To first order, the density of available occupied donors is $N_D F(\zeta_g) k_B T$, which is equal to $3N_A k_B T / E_D$ by Eq. (A2) and (2.7). This result, when combined with the phonon involvement, yields the dependence shown in Eq. (2.13).

In the high-temperature approximation, the transition rate is limited by the number of available final states, i.e., the N_A vacant donors. This result, when combined with the phonon involvement, yields the dependence shown in Eq. (2.14).

III. COMPARISON OF THEORY AND EXISTING DATA

A. Hopping as the only narrowing mechanism

Combining Eqs. (1.1), (C3), and substituting the low- T , low- K approximation for ω_h as given by Eq. (2.13), one obtains for the theoretical linewidth

$$\Delta H_{\text{theor}} = \frac{8\pi e^2 g \mu_B [\Delta H_0^2 + \frac{4}{3} I(I+1) H_0^2]}{9D \sqrt{3} \kappa_0} \frac{N_D R_D^2}{N_A (k_B T)^2}. \quad (3.1)$$

1. Donor concentration dependence

If the acceptor concentration is assumed to be nearly constant, as one would expect for samples with no deliberate acceptor doping, the theory predicts that $\Delta H_{\text{theor}} \propto 1/R_D$. The data in Refs. 1, 2, and 4 show that the observed linewidth (ΔH_{exp}) increases exponentially with R_D for lightly doped samples. Thus, the theory of hopping does not predict the proper donor dependence.

2. Temperature dependence

For temperature-dependence comparisons, 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 obtained from experimental data as

$$\omega_N = \frac{(2/\sqrt{3})g\mu_B[\Delta H_0^2 + \frac{4}{3}I(I+1)H_0^2]}{\Delta H_{\text{exp}}} = \frac{\text{constant}}{\Delta H_{\text{exp}}} \quad (3.2)$$

The constant is derived for different donors from the information in Table I of Appendix C.

A conversion of the data in Refs. 2 and 4 has been done and results are plotted in Figs. 1 and 2. Each data curve shows that ω_N is nearly linear in T for these data. However, since the samples

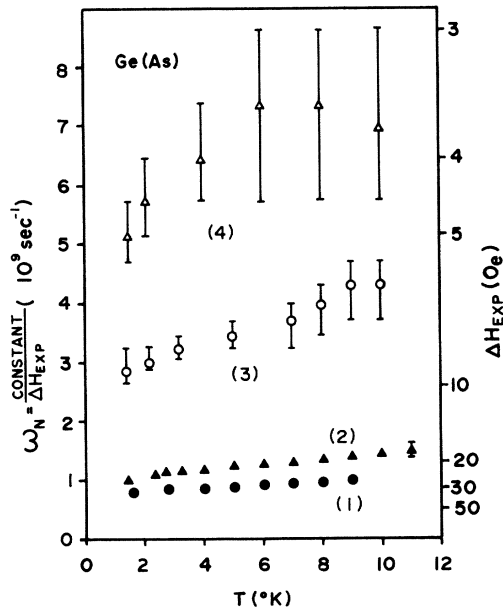


FIG. 1. Plot of ω_N vs temperature for arsenic-doped germanium. Data are calculated from Ref. 4, where the donor concentrations were given as (1) $3.4 \times 10^{16} \text{ cm}^{-3}$; (2) $4.6 \times 10^{16} \text{ cm}^{-3}$; (3) $7.0 \times 10^{16} \text{ cm}^{-3}$; and (4) $1.8 \times 10^{17} \text{ cm}^{-3}$.

were not compensated, $T \ll T_c$ and Eq. (2.13) predicts that ω_h should be quadratic in T . In addition, the positive $T=0$ intercept for ω_h is inconsistent with the theory.

3. Acceptor concentration dependence

For low K , ΔH should have a N_A^{-1} dependence. Since previous forms for ΔH did not really consider the influence of acceptor concentration, virtually no data exists. However, consistency of results from different laboratories suggest no strong N_A dependence for low K .

B. Combined exchange and motional narrowing

From the previous remarks it is clear that if hopping is contributing to the narrowing, it cannot be the only narrowing mechanism. Some other mechanism must be present. Furthermore, the second mechanism must be dominating the hopping mechanism since the data clearly show a donor dependence, temperature dependence, $T=0$ intercept and apparently lacks an acceptor concentration dependence for low K .

Other authors^{2,4,5,13} have investigated the problem of donor ESR spectral narrowing by assuming that exchange is the narrowing mechanism. Since the exchange mechanism could cause many of the observed features,^{28,32,33} combined exchange and motional narrowing have been considered.

Appendix D shows that if exchange was the dominant mechanism, then the total predicted narrow-

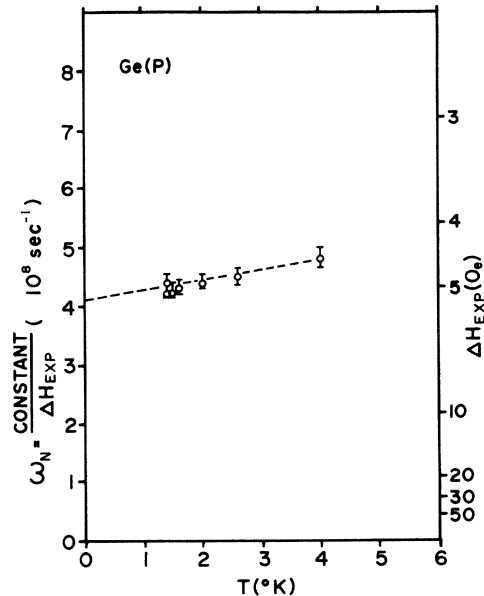


FIG. 2. Plot of ω_N vs temperature for phosphorus-doped germanium. Data are from Ref. 2 with $N_D = 8 \times 10^{16} \text{ cm}^{-3}$.

ing frequency would be

$$\omega_T = \omega_e + \omega_N/\pi, \quad (3.3)$$

where $\omega_e = J/\hbar$ is the exchange frequency. Without precisely calculating J , some conclusions can be drawn concerning this result by supposing that the $T=0$ intercept of an ω_N vs T curve is ω_e . Substitution of ω_N ($T=0$) values for ω_e and the low- T , low- K expressions for ω_h [Eq. (2.13)] yields

$$\omega_T = \omega_N(T=0) + CN_A T^2 / N_D^{1/3}, \quad (3.4)$$

where C is a constant.

Upon comparison of ω_T with the ω_N data in Figs. 1 and 2, it appears unlikely that hopping is causing even the temperature-dependent part of ω_T since the temperature-dependent data does not appear to be quadratic in T . Even if an attempt to fit Eq. (3.4) to the data in Fig. 1 is made, the unlikely assumption that N_A increases with N_D ³¹ is necessary.

Also, a combination of exchange and hopping narrowing does not predict the effect observed in a compensated sample. Data⁵ on an $N_D = 1.2 \times 10^{16}$ cm⁻³ and $K = 0.4$ sample showed that narrowing decreases with increasing N_A and constant N_D and T . This data is compatible with exchange narrowing. However, it is not compatible with the fact that hopping should increase with increasing N_A and should eventually dominate the exchange narrowing. [Using Eq. (1.1), the parameters for Ge(As) as given above and in Table I, and computer calculations for ω_h without the low- K approximation,³¹ one finds that, at $T = 1^\circ\text{K}$, $\omega_h = 6.7 \times 10^8$ sec⁻¹, while at $T = 2^\circ\text{K}$, $\omega_h = 4.9 \times 10^9$ sec⁻¹. This means that significant narrowing should have been observed at all but the lowest of temperatures.]

C. Best conditions for observing motional narrowing effects

There seems no reason for believing that hopping is not a valid physical process. Indeed, it has been used to explain the resistivity of semiconductors at low donor concentrations.²⁸ Furthermore, the change of hyperfine state that accompanies hopping could affect the ESR spectrum. Our results indicate that the influence of hopping should be sought in samples with low donor concentration, at low temperature, and with moderate compensation ($K \approx 0.5$). The low N_D ensures validity of the Miller and Abrahams hopping process. The low T keeps most donor electrons in the ground states. Moderate compensation is needed to obtain an appreciable value for ω_h .

IV. DISCUSSION AND CONCLUSIONS

This work was initiated because several non-rigorous theoretical treatments have been invoked

to "determine" if hopping was producing line narrowing in doped semiconductors. Most previous workers,^{1,2,4,11} believed that the averaged hopping transition rate was

$$\omega_h = U_{ij}(R_D, \Delta) = \frac{1}{B} R_D^{3/2} e^{-2R_D/a} \frac{\Delta}{1 - e^{-\beta\Delta}}, \quad (4.1)$$

which is actually an unaveraged transition rate between one particular pair of donors separated by an average distance R_D [see Eq. (2.3)]. The quantity Δ (actually Δ_{ij}) was referred to as the "activation energy for hopping." (Once,¹³ Δ was replaced by the activation energy for impurity conduction.) Also, we note that, in effect, a high compensation ratio is tacitly assumed. In addition, when the above ω_h was used in Eq. (1.1), values other than the precise ΔH and $\langle H^2 \rangle_{av}$ were used. (See Appendix C.)

Equation (4.1) seems to agree with the data because of (i) its almost exponential dependence on R_D , (ii) a value of $\Delta \approx 0.34$ – 0.54 meV fits a range of the data,² and (iii) $\Delta > 0$ yields an $\omega_h \neq 0$ at $T = 0$. However, there are numerous reasons why the theoretical basis for Eq. (4.1) is not very satisfactory. First, an ensemble average was not taken. Second, there is no N_A dependence since the distribution of electrons was not used. Third, the distribution of impurities was not used. Fourth, only excitation due to phonons at one frequency is involved. A more detailed critique of Eq. (4.1) has been given elsewhere.³¹

Recently,⁵ rather extensive data in Ge(As) has been taken. It was concluded that electron motion, which would include phonon-induced tunneling, is not an effective narrowing mechanism. This conclusion, however, was based on the belief that ω_h should be proportional to an exponential function containing an activation energy. As we have noted, neither Eq. (2.13) or Eq. (2.14) predict an activation-energy dependence.

In summary, the motional narrowing frequency due to hopping has been calculated [Eq. (2.8)]. For low compensation ratios, this frequency can be reasonably approximated by the low-temperature result [Eq. (2.13)] or the high-temperature result [Eq. (2.14)]. These latter two equations explicitly show the dependence on donor concentration, acceptor concentration, and temperature. The origin of these dependences has been discussed and is now well understood. For many years, all three of these dependences were presumed to be entirely different.

With our new understanding, we have been able to conclude that: (i) hopping is not the only mechanism causing the line narrowing; (ii) hopping in combination with exchange does not agree well with the existing data; (iii) at this time there is no good

evidence that hopping is influencing the spectrum at all; (iv) to search for hopping effects in ESR spectra one should look at low temperatures in samples with low donor concentrations and moderate compensation ratios.

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APPENDIX A: CALCULATION OF THE GROUND-STATE FERMI ENERGY

Equation (2.5) is used to define the Fermi energy in terms of N_A, N_D , and T or, equivalently, in terms of E_A, K , and T . The defining equation may be written as²⁸

$$K = \int_0^\infty \frac{F(E)dE}{1 + e^{-\beta(E-\zeta_F)}}, \quad (\text{A1})$$

where $F(E)$ is the density of states given by Eq. (2.7). Equation (A1) may be solved numerically if a numeric solution of Eq. (2.8) is needed.³¹ However, it may also be solved analytically, using certain approximations which are also used in the evaluation of ω_h in Sec. II E.

In the analytical calculation, two approximations may be made. The first is the low-temperature approximation as considered by Miller and Abrahams.²⁸ They integrated Eq. (A1) once by parts and considered the resulting product of electron distribution functions, $\{[1 + e^{-\beta(E-\zeta_F)}][1 + e^{\beta(E-\zeta_F)}]\}^{-1}$, to be sharply peaked at $E = \zeta_F$. Their results were

$$\zeta_F = \frac{E_A}{[-\ln(1-K)]^{1/3}} \approx E_D. \quad (\text{A2})$$

It can be shown³¹ that the first equality in Eq. (A2) is valid for all K if

$$T \ll \frac{E_A}{10.6k_B[-\ln(1-K)]^{4/3}} = T_C. \quad (\text{A3})$$

The second equality of Eq. (A2) is valid in the low- T limit if the compensation is low.

In the higher-temperature limit, the $[1 + e^{-\beta(E-\zeta_F)}]$ function can be removed from the integral in Eq. (A1) and evaluated at $E_0 = (3/4)^{1/3}E_A$ if $F(E)$ is considered sharply peaked at E_0 . Integrating $F(E)$, one then obtains

$$K = \frac{1}{1 + e^{-\beta(E_0-\zeta_F)}}. \quad (\text{A4})$$

Thus,

$$\zeta_F = E_0 + k_B T \ln \frac{(1-K)}{K}. \quad (\text{A5})$$

The criterion for validity of this procedure is³¹

$$T \gg \frac{0.66E_A}{k_B} (1-K) \equiv T'_C. \quad (\text{A6})$$

For $N_A \approx 10^{14} \text{ cm}^{-3}$ and $N_D \approx 10^{16} \text{ cm}^{-3}$, $T_C \approx 300 \text{ }^\circ\text{K}$ and $T'_C \approx 5 \text{ }^\circ\text{K}$.

APPENDIX B: CALCULATION OF THE Δ ENERGY DISTRIBUTION FUNCTION

The purpose of this appendix is to find a $G(\Delta_{ij})$ such that the special integration over θ discussed with Eq. (2.6) will be converted to one over $2G(\Delta_{ij})d\Delta_{ij}$. Here $G(\Delta_{ij})$ is a normalized distribution of values of ground-state-energy differences Δ_{ij} if the separation of donors i and j is r_{ij} and the ground-state energy of donor i is $E_i = e^2/\kappa_0 r_{iA}$. Now the relation for this variable change may be written as

$$G(\Delta_{ij}) = \frac{1}{2} \sin\theta \frac{d\theta}{d\Delta_{ij}} = -\frac{1}{2} \frac{d(\cos\theta)}{d\Delta_{ij}}, \quad 0 < \theta < \pi. \quad (\text{B1})$$

Thus, if a relation between $\cos\theta$ and Δ_{ij} can be found, $G(\Delta_{ij})$ may be calculated.

Although $G(\Delta_{ij}) = G(\Delta_{ij}, r_{ij}, E_i)$, in the present calculation r_{ij} and E_i can be considered as fixed constants. The fixing of these parameters fixes the two sides (r_{ij} and r_{iA}) of a triangle formed by i, j , and the nearest acceptor A . A relation between Δ_{ij} and θ may then be written as

$$\Delta_{ij} = E_i - E_j = \frac{e^2}{\kappa_0} \left(\frac{1}{r_{iA}} - \frac{1}{(r_{iA}^2 + r_{ij}^2 - 2r_{iA}r_{ij}\cos\theta)^{1/2}} \right), \quad (\text{B2})$$

by use of the law of cosines. Hence, with Eq. (B1) and the value for θ from Eq. (B2), one may write, dropping the subscripts,

$$G(\Delta) = \frac{e^3}{2\kappa_0 E^2 r} \frac{1}{[1 - (\Delta/E)]^3}, \quad \Delta^- < \Delta < \Delta^+, \quad (\text{B3})$$

where Δ^- corresponds to $\theta = 0$ and Δ^+ corresponds to $\theta = \pi$. If $0 < r < e^2/\kappa_0 E$, then

$$\Delta_1^- = \frac{-Er}{[(e^2/\kappa_0 E) - r]}, \quad \Delta_1^+ = \frac{Er}{[(e^2/\kappa_0 E) + r]}. \quad (\text{B4a})$$

If $e^2/\kappa_0 E < r < \infty$, then

$$\Delta_2^- = \frac{-E[2e^2/\kappa_0 E - r]}{r - e^2/\kappa_0 E}, \quad \Delta_2^+ = \frac{Er}{[(e^2/\kappa_0 E) + r]}. \quad (\text{B4b})$$

APPENDIX C: CALCULATION OF THE MEAN-SQUARE BREADTH OF A NON-NARROWED SPECTRUM

The $\langle H^2 \rangle_{av}$ quantity may be calculated by using a normalized probability distribution, $P(H)$, which describes the shape of the non-narrowed spec-

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

Doping element	Germanium ^a		
	As	Bi	P
$\langle H^2 \rangle_{av}$ (Oe ²)	1.63×10^3	9.05×10^4	1.35×10^2

^aComputed from data in Ref. 1. The data for Ge(Sb) are complicated by strain effects (Refs. 1, 2, 34, 35).

trum.²⁷ The $n = 2I + 1$ donor lines are assumed to be equal in strength and of the same Gaussian shape with a mean-square spread of ΔH_0 , and regular interval spacing of $2H_0$. Hence, a normalized distribution for this spectrum can be written as

$$P(H) = \sum_{\substack{m=-(n-1) \\ (m \text{ odd})}}^{n-1} \frac{1}{n(2\pi\Delta H_0)^{1/2}} \exp\left(\frac{-(H-mH_0)^2}{2(\Delta H_0)^2}\right), \quad (C1)$$

where H is measured relative to the center of the spectrum. Thus

$$\begin{aligned} \langle H^2 \rangle_{av} &= \int_{-\infty}^{\infty} H^2 P(H) dH \\ &= (\Delta H_0)^2 + \frac{2}{n} \sum_{m=1,3,5,\dots}^{n-1} m^2 H_0^2. \end{aligned} \quad (C2)$$

Performing the summation over m with $n = 2I + 1$, one obtains

$$\langle H^2 \rangle_{av} = (\Delta H_0)^2 + \frac{4}{3} I(I+1) H_0^2. \quad (C3)$$

Table I shows values of $\langle H^2 \rangle_{av}$ for isolated donor ESR spectra computed from Eq. (C3). In most cases the $(\Delta H_0)^2$ term can be neglected except when $I = \frac{1}{2}$.

APPENDIX D: LINEWIDTHS IN THE PRESENCE OF EXCHANGE AND MOTIONAL NARROWING

The width $\Delta\omega$ in frequency units of a narrowed line in the theory of Anderson and Weiss²⁶ and Anderson²⁷ is the coefficient of τ in the expression

$$\frac{1}{2} \langle X^2 \rangle_{av} = \langle \omega^2 \rangle_{av} \int_0^\tau (\tau - t) \phi_{\Delta\omega}(t) dt. \quad (D1)$$

Here, $\langle \omega^2 \rangle_{av}$ is the average square spread of the non-narrowed frequency spectrum and $\phi_{\Delta\omega}(t)$ is the correlation function of the random modulation. If exchange narrowing and motional narrowing are independent effects and hence additive,

$$\phi_{\Delta\omega}(t) = e^{(i\pi\omega_e^2 t^2 - \omega_h t)}, \quad (D2)$$

where $\omega_e = J/\hbar$ is the exchange frequency and ω_h is the motional frequency. For $\frac{1}{2}\omega_e\tau\sqrt{\pi} \gg 1$, then

$$\frac{1}{2} \langle X^2 \rangle_{av} \approx A + \frac{\tau \langle \omega^2 \rangle_{av}}{\omega_e} e^{\omega_h^2/\omega_e^2\pi} \operatorname{erf}(\omega_h/\omega_e\sqrt{\pi}), \quad (D3)$$

where A is independent of τ . Thus, in magnetic field units,

$$\Delta H = \frac{\hbar\Delta\omega}{g\mu_B} = \frac{g\mu_B \langle H^2 \rangle_{av}}{\hbar\omega_e} e^{\omega_h^2/\omega_e^2\pi} \operatorname{erf}(\omega_h/\omega_e\sqrt{\pi}). \quad (D4)$$

When exchange narrowing dominates, i.e., $\omega_h/\omega_e\sqrt{\pi} \ll 1$,

$$\Delta H \approx \frac{g\mu_B \langle H^2 \rangle_{av}}{\hbar(\omega_e + \omega_h/\pi)}; \quad (D5)$$

while, when motional narrowing is dominant, i.e., $\omega_h/\omega_e\sqrt{\pi} \gg 1$,

$$\Delta H \approx \frac{g\mu_B \langle H^2 \rangle_{av}}{\hbar(\omega_h + \pi\omega_e^2/\omega_h)}. \quad (D6)$$

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