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Spin Resonance of Localized and Delocalized Electrons in Phosphorus-Doped Silicon between 20 and 30 °K

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Electron spin resonance has been studied in phosphorus-doped silicon from 20 to 300 °K in a donor concentration range ($7.5\times10^{14}\,\mathrm{cm}^{-3}\leqslant N_D\leqslant8\times10^{16}\,\mathrm{cm}^{-3}$), where exchange interactions between donor atoms are negligible. In the lower limit of the temperature range used, most of the donor electrons are bound in the ground state of the donor atoms and the two lines of the hyperfine structure are observed. It is shown that the broadening of these lines at $T\approx30$ °K is determined by the exchange scattering between the donor electrons and the conduction electrons, while their shift arises from the thermal excitation to the first excited level. From the broadening, we obtain the value of the exchange cross section ($\sigma_{\mathrm{ex}}=0.35\times10^{-12}\,\mathrm{cm}^2$). At higher temperatures, a single line is observed which narrows when the temperature increases (in the region $50\,°\mathrm{K}\lesssim T\lesssim75\,°\mathrm{K}$). This narrowing is attributed to the motional averaging of the hyperfine interaction. In the intermediate temperature region ($75\,°\mathrm{K}\lesssim T\lesssim150\,°\mathrm{K}$), it is shown that the dominant relaxation mechanism arises from the spin-orbit interaction in the first excited level modulated by the thermal motion of the electrons. In the high-temperature region ($150\,°\mathrm{K}\lesssim T\lesssim300\,°\mathrm{K}$), where most of the electrons are excited into the conduction band, the value and the temperature dependence of the linewidth are well accounted for by the theories of Yafet and Elliott on spin relaxation of conduction electrons. The observed behavior of the spin resonance is quantitatively explained over the whole range of temperatures and concentrations studied, using only two adjustable parameters.

I. INTRODUCTION

The electron spin resonance in n-type silicon has so far been extensively studied mainly in the liquid-helium temperature region.[1] At these temperatures, the donor electrons are bound in the ground state of the donor atoms and the resonance studies have given precise information on this state. At higher temperatures, the donor electrons are thermally excited into bound donor states and Bloch states of the conduction band. Thus, these electrons are distributed over several orbital states and may undergo magnetic interactions different in size and nature in these states. Our purpose is to explain quantitatively the spin-resonance behavior of this system. Some experimental results have been obtained by others[2,3] for relatively high values of the donor concentration N_D ($N_D>10^{17}\,\mathrm{cm}^{-3}$). At these concentrations, however, the additional complication due to exchange interaction between donor atoms as well as impurity band effects[4,5] makes the interpretation of the results difficult. Our study is therefore purposely restricted to the region of low donor concentrations for which zero interaction between the spins of the donors may be assumed. Our samples are doped with phosphorus ($7.5\times10^{14}\,\mathrm{cm}^{-3}\leqslant N_D\leqslant8\times10^{16}\,\mathrm{cm}^{-3}$); the temperature range used extends from 20 to 300 °K.

In these ranges, the main features of the resonance spectrum can be sketched as follows. At $T\approx20$ °K, one observes a well-resolved hyperfine structure, characteristic of fixed noninteracting centers. When the temperature rises above ≈ 30 °K, the two lines of the hyperfine structure broaden and then vanish (at $T\approx40$ °K). At slightly higher temperatures ($T\approx50$ °K), a single central line appears with a Lorentzian shape. This line begins to narrow with increasing temperature, goes through a minimum width at $T\approx100$ °K, and then rapidly broadens when T approaches 300 °K.

The statistical distribution of the electrons over their different possible states is an essential parameter to explain these experimental facts. We calculate this distribution in Sec. II, using the well-known energy-level scheme for the phosphorus atom in silicon.[6] Then we give a preliminary description of the resonance results in Sec. III. Sections IV and V are devoted to the interpretation of these results. In Sec. IV, we explain the two striking effects observed in the temperature region where the hyperfine structure is still resolved ($T\lesssim40$ °K): the broadening and the shift of the hyperfine lines when the temperature increases. In Sec. V, we give a model which accounts for all the characteristics of the resonance line in the temperature region where the hyperfine structure is not resolved and a single line is observed ($T\gtrsim50$ °K). Two adjustable parameters only are used to calculate the linewidth which results from the different spin-relaxation mechanisms involved in the model. We show in conclusion that this theoretical linewidth is in satisfactory agreement with the experimental linewidth over the whole range of temperature and donor concentration used.

II. ELECTRONIC DISTRIBUTION OVER DONOR AND CONDUCTION-BAND STATES

In the effective-mass formulation, one obtains six-fold degenerate 1*s* hydrogenlike orbitals for the ground state of the donor atom in silicon. When the tetrahedral symmetry of the true impurity potential is taken into account, this ground state splits[6] into a singlet state A_1, a doublet state E, and a triplet state T_2. The doublet and triplet levels are very close to one another and they are separated from the ground level A_1 by the "valley-orbit" splitting Δ ($\Delta \approx 11\times 10^{-3}$ eV, in the case of phosphorus).[7-9] The other excited states lie well above these 1*s* states (see Fig. 1). In this paper, the ground state A_1 is denoted by (0), and the 1*s* states, E and T_2, collectively by (1); the successive higher energy states are labeled by 2, 3, 4, ... Strictly speaking, there is a small temperature dependence of the energy levels.[10] In view of the weakness of this effect, these levels will be taken as temperature independent in the following calculation.

It is shown[11] that the statistical distribution over the donor and conduction-band states is described by the following equations:

$$n_c = N_c e^{E_F/kT} \ , \tag{1a}$$

$$n_j = N_D[g_j e^{(E_F-E_j)/kT}/(1+\textstyle\sum_i g_i e^{(E_F-E_i)/kT})] \ , \tag{1b}$$

$$N_D - N_A = n_c + \textstyle\sum_j n_j \ , \tag{1c}$$

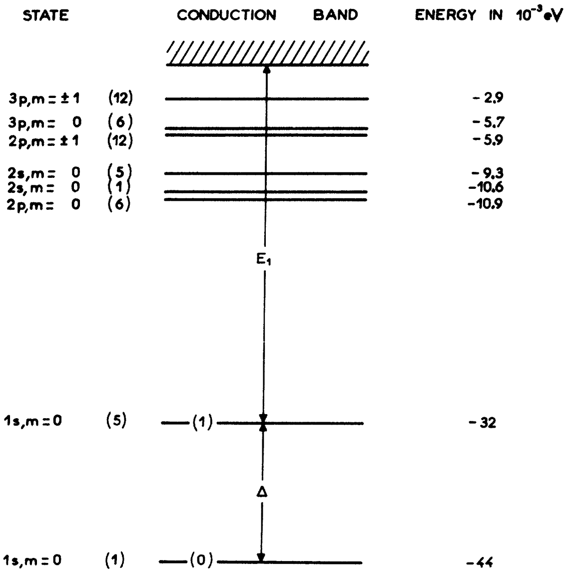

FIG. 1. Energy-level diagram for a phosphorus impurity in silicon. The five 1*s* excited states are denoted collectively by (1) and are taken to have the same energy E_1. They are separated from the ground state (0) by the "valley-orbit" splitting Δ.

where n_c, n_j are, respectively, the concentrations of electrons in the conduction band and the donor level j; E_j and g_j are the energy and degeneracy (including spin) of the jth level (the energies E_j are counted from the conduction-band edge); N_c is the equivalent density of states for the conduction band; N_D and N_A are the donor and acceptor concentrations. Since the Fermi level E_F lies well above the valence band, all the acceptor levels are filled and the net number of electrons shared between the conduction band and the donor states is $(N_D - N_A)$, as expressed by Eq. (1c). The summations in Eq. (1a) and (1b) are restricted to those levels which are separated from the conduction band by more than the energy kT. In these summations it is a very good approximation in the temperature range of interest to keep only the terms related to the ground state (0) and the 1*s* excited states (1). In this "three-level" scheme the ratios $n_0/(N_D - N_A)$, $n_1/(N_D - N_A)$, and $n_c/(N_D - N_A)$ are explicitly calculated and plotted as a function of temperature in Figs. 2(a)-2(c). According to these figures, three temperature regions can be distinguished: a low-temperature region ($T \lesssim 75$ °K), where the electrons are mainly trapped in the ground state of the donors; a high-temperature region ($T \gtrsim 150$ °K) where almost all the donor electrons are excited into the conduction band; and an intermediate temperature region (75 °K $\lesssim T \lesssim$ 150 °K), where the population of the 1*s* excited states goes through a maximum. In Fig. 2(b) the rather large value of this maximum can be seen for the more heavily doped samples.

III. EXPERIMENTAL PROCEDURE AND RESULTS

The spin-resonance experiments are performed using a conventional bridge-type spectrometer operating at X band with high-frequency magnetic field modulation (100 kHz). All the samples used are doped with phosphorus. One of them is compensated with boron (see Table I). Since the samples are single crystals, the surface-to-volume ratio is small so that the surface state line[12] is insignificant and is completely removed by etching the sample with CP_4.

In the concentration range of interest, the donor electron resonance spectrum at liquid-helium temperature exhibits two lines due to the hyperfine interaction $A\vec{I}\cdot\vec{S}$ between the donor electron spin $\vec{S}$ and the phosphorus nucleus spin $\vec{I}$ ($I=\frac{1}{2}$). The separation of these lines (42 G) corresponds to a magnitude of the hyperfine interaction, $A = 8\times 10^8$ sec^{-1}. Their Gaussian shape and their width result from the hyperfine coupling of the donor electron with the Si^{29} nuclei randomly distributed on the lattice

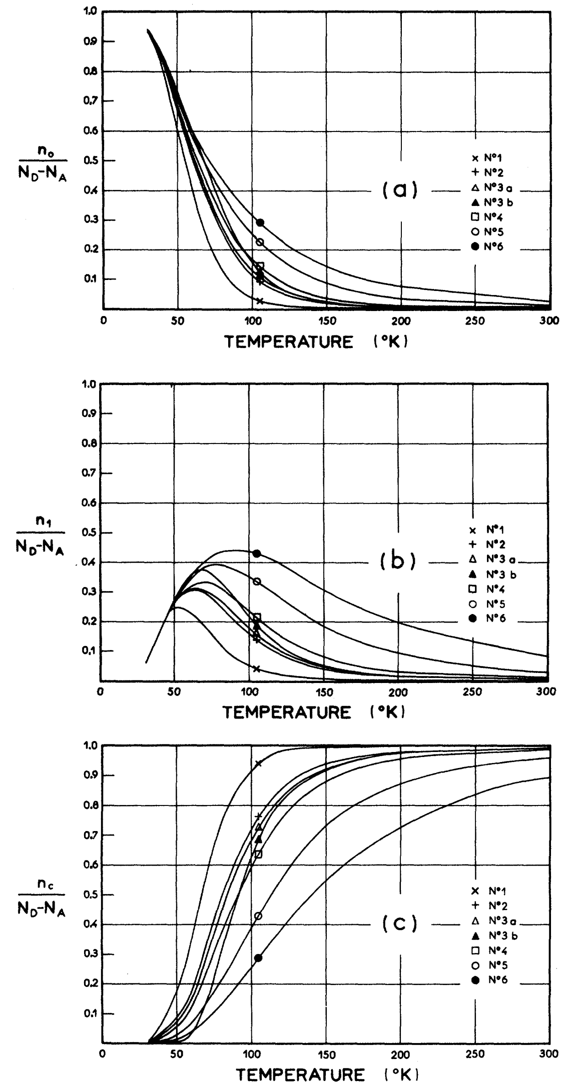

FIG. 2. Relative number of donor electrons, (a) in the ground level (0), (b) in the intermediate level (1), (c) in the conduction band. The characteristics of the samples are given in Table I. We note that: (i) At low temperatures, almost all the donor electrons are trapped in the donor's ground state; (ii) at intermediate temperatures, the occupation degree of the intermediate level (1) goes through a maximum; (iii) at high temperatures, almost all the donor electrons are excited into the conduction band. We note also that the ionization is more complete when the donor concentration is small.

sites (standard deviation of the Gaussian distribution is 1.07 G).[1] The hyperfine spectrum remains resolved up to about 40 °K. When the temperature approaches this value, the hyperfine lines move toward one another (see Fig. 3) and simultaneously rapidly broaden (see Fig. 4). From $T \approx 50$ °K up to room temperature, the resonance spectrum exhibits a single Lorentzian line. As illustrated by Fig. 5, the width of this line is a function of temperature and concentration. For all the samples used the linewidth goes through a minimum at intermediate temperatures ($T \approx 100$ °K). Except at low temperatures ($T \approx 50$ °K), it is a monotonic increasing function of the donor concentration. At room temperature, however, this concentration dependence tends to disappear. Between the two temperature regions where two well-separated lines or a single line are observed (40 °K $\lesssim T \lesssim$ 50 °K), we cannot detect any signal. This is due to the fact that the hyperfine lines rapidly broaden before they merge into a single line, so that the signal-to-noise ratio becomes too poor for the resonance signal to be observed. Fortunately, the corresponding temperature region is narrow. No appreciable variation of the g factor is observed in the whole range of temperature and concentration employed. A constant value is found, $g \approx 1.999$, in agreement with measurements made by Kodera at 77 and 300 °K on more heavily doped samples.[3]

IV. HYPERFINE STRUCTURE RESOLVED: MOTIONAL EFFECTS ON RESONANCE SPECTRUM

The quantitative features of the hyperfine spectrum (width and separation of the lines) observed at very low temperatures are altered when the temperature rises above ≈ 30 °K. As the hyperfine interaction is large in the donor ground state and very weak or zero in the other states (donor excited states and conduction-band states), the motion of the electrons between these states gives rise to a modulation of this interaction. We show in this section that at $T \approx 30$ °K, the motion of the electrons becomes rapid enough to affect the resonance spectrum. The shift of the lines when the temperature rises has been experimentally studied by others[13]; however, the broadening is a much more striking effect, and studying its temperature and concentration dependence gives a direct way to obtain the parameters of motion.

Several mechanisms of motion are to be considered: (i) *thermal excitation of the electron from*

TABLE I. Characteristics of the samples used.

Sample No.	Phosphorus concentration N_D in cm^{-3}	Boron concentration N_A in cm^{-3}	Room-temperature resistivity in Ω cm
1	7.4×10^{14}	···	4.5
2	3.7×10^{15}	···	1.3
3a	4.5×10^{15}	···	0.9
3b	4.5×10^{15}	2.8×10^{15}	2.4
4	7.8×10^{15}	···	0.6
5	2.7×10^{16}	···	0.2
6	$8\ \times10^{16}$	···	0.1

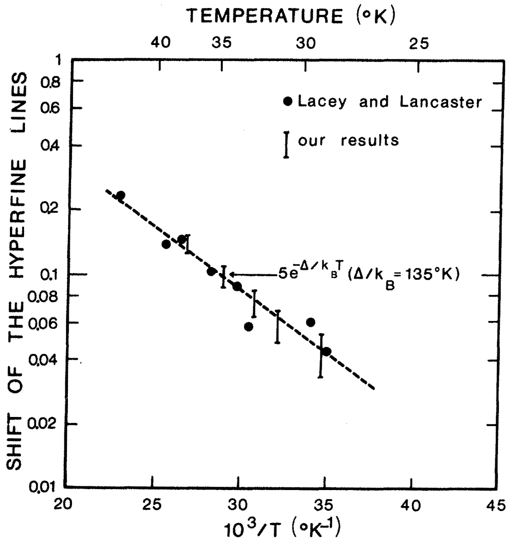

FIG. 3. Temperature dependence of the relative shift of the hyperfine lines $\delta/(A/2\gamma_e)$. Our experimental values and also those obtained by Lacey and Lancaster (Ref. 13) are indicated.

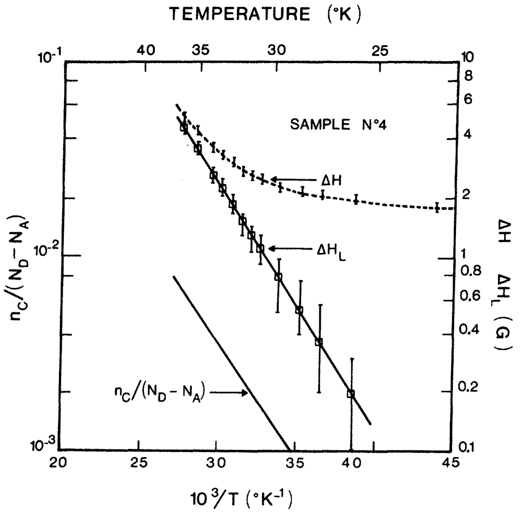

FIG. 4. Dashed curve shows the measured values of the width of the hyperfine lines ΔH which is the peak-to-peak width of the first derivative of the absorption curve multiplied by $\frac{1}{2}\sqrt{3}$. ΔH_L is one-half of the width at half-height of the Lorentzian components of the hyperfine lines computed from the values of ΔH as described in the Appendix. The relative number of electrons in the conduction band $n_c/(N_D-N_A)$ is also plotted as a function of $1/T$.

the ground level to the excited levels of the donor atom. The essential feature of this process is that it leaves the electron bound to the same donor center. Its effect on the hyperfine spectrum (shift and broadening of the lines) will be investigated in Sec. IV A. As the upper excited levels (2), (3), etc., are lying well above the level (1), thermal excitation to this latter level should be most predominant and it, only, will be considered. (ii) *Exchange scattering and thermal excitation to the conduction band*. In contrast with the previous process, the exchange scattering between the donor electron and the conduction electrons and the thermal excitation into the conduction band give rise to a delocalization of the donor electron. The effects of these processes on the hyperfine spectrum will be investigated in Sec. IV B.

A. Thermal Excitation to First Excited Level

In this process, the donor electron remains bound to the same donor center and experiences successively the values of the hyperfine field in levels (0) and (1): $+A/2\gamma_e$ (or $-A/2\gamma_e$) and zero, respectively. (γ_e is the electronic gyromagnetic ratio.) Thus, the electron resonance frequency oscillates between two values: $\omega_0+A/2$ (or $\omega_0-A/2$) in the ground level (0), and ω_0 in the level (1). The rate of the jumping from $\omega_0\pm A/2$ to ω_0 is the rate of thermal excitation from level (0) to level (1), ω_{01}. The inverse transition rate ω_{10} characterizes the rate of the jumping from ω_0 to $\omega_0\pm A/2$ and is related to ω_{01} by detailed balance

$$n_0\omega_{01}=n_1\omega_{10} \; .$$

From Anderson's theory,[14] we know that a single resonance line will be observed if at least one of the jumping rates, ω_{01}, ω_{10}, is larger than the separation between the values of the resonance frequency, $A/2$ (rapid motion of the spins). Previous

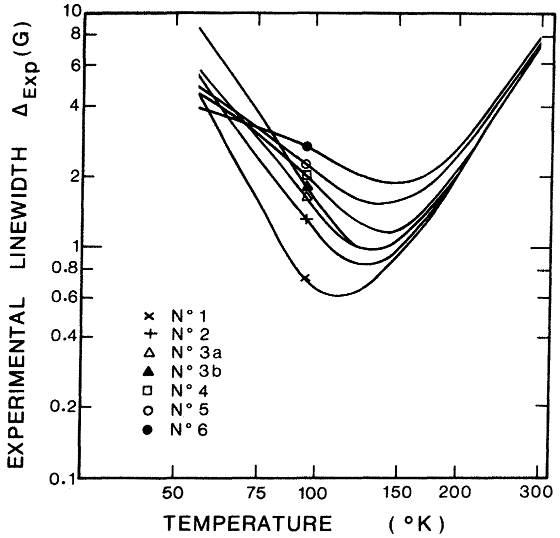

FIG. 5. Temperature dependence of the experimental linewidth Δ_{Exp} of the single line observed at $T \gtrsim 50$ °K.

theoretical and experimental estimates of the decay rate ω_{10} ensure that this condition is actually fulfilled.[15] One then readily shows that the resonance line is shifted from its original position by an amount δ, which is given by

$$\delta = (A/2\gamma_e)(n_1/n_0+n_1) \simeq (A/2\gamma_e)(5e^{-\Delta/k_BT}) . \qquad (2)$$

The above equation merely expresses that the actual resonance frequency of the electron is the average value of the resonance frequencies in levels (0) and (1), weighted by the relative populations in these levels. The random modulation of the hyperfine interaction also gives rise to a broadening of the hyperfine lines ΔH_L (1s excitation), which is expressed by

$$\Delta H_L(1s \text{ excitation}) = (A^2/4\gamma_e\omega_{10})(n_1/n_0+n_1)$$

$$\simeq (A^2/4\gamma_e\omega_{10})(5e^{-\Delta/k_BT}) . \qquad (3)$$

In deriving Eqs. (2) and (3) we have assumed that the hyperfine lines were infinitely narrow in the absence of motional effects. As explained in Sec. III, they are, in fact, Gaussian distributions of extremely narrow Lorentzian curves. Equations (2) and (3), respectively, describe the shift and the broadening of these individual components of the hyperfine lines.

Owing to the relatively large value of the decay rate ω_{10} $(\omega_{10} > A)$, thermal excitation to level (1) does not significantly contribute to the broadening of the hyperfine lines.[16] On the other hand, the process is responsible for the shift of these lines. As shown by Fig. 3, the value and the temperature dependence of the relative shift $\delta/(A/2\gamma_e)$ are well predicted by Eq. (2).

B. Exchange Scattering and Thermal Excitation to Conduction Band

We consider now the two other modulation processes of the hyperfine interaction: the thermal excitation of the donor electron into the conduction band and the exchange scattering of the donor electron by a conduction electron. Both these processes allow a given electron to go from one donor site to another through the conduction band and thus successively to "feel" the three possible values of the hyperfine field $+A/2\gamma_e$, 0, and $-A/2\gamma_e$.

We denote by ω_{0c} and ω_{ex} the excitation rate and the exchange rate, respectively. The excitation rate ω_{0c} concerns individual donor atoms and does not depend on the donor concentration. On the other hand, the exchange rate ω_{ex} which is related to the exchange cross section σ_{ex} by

$$\omega_{ex} = \sigma_{ex} v n_c , \qquad (4)$$

is proportional to the conduction-electron concentration n_c (v is the average velocity of the conduction electrons). When the donor electron is excited into the conduction band, or when it is exchanged with a conduction electron, its resonance frequency ω jumps from $\omega = \omega_0 \pm A/2$ to $\omega = \omega_0$, where ω_0 is the resonance frequency in the absence of hyperfine interaction. The rate of the jumping Ω is given by

$$\Omega = (\omega_{0c} + \omega_{ex}) \qquad (5)$$

and depends only on the donor concentration through the exchange rate ω_{ex}. The rate of the jumping Ω' from ω_0 to $\omega_0 \pm A/2$ is related to Ω by detailed balance

$$n_0 \Omega = 2 n_c \Omega' .$$

Using the jumping rates Ω, Ω' to describe the motion of the spins, we obtain the shape $I(\omega)$ of the absorption spectrum by a straightforward application of the theory of Anderson[14,17]:

$$I(\omega) = \frac{\omega^2[p(\Omega+\Omega')A^2 - \Omega' A^2/2] + [\Omega^2 + 2\Omega\Omega' + (1-2p)A^2/4]\Omega' A^2/2}{[2\omega^2(\Omega+\Omega') - \Omega' A^2/2]^2 + \omega^2[2\Omega\Omega' + \Omega^2 - \omega^2 + A^2/4]^2} . \qquad (6)$$

The origin of the frequency scale has been taken at the resonance frequency ω_0 and the relative occupation of the ground state is denoted by $2p$. This expression allows a quantitative description of the resonance spectrum for all the values of the jumping rates Ω, Ω'. One then readily shows that the hyperfine spectrum remains resolved and consists of two Lorentzian lines as long as the jumping rate Ω remains smaller than the hyperfine interaction ($\Omega < A$; slow motion of the spins). With the appropriate simplifications in this case, one obtains from Eq. (6) the width of the lines due to the delocalization of the electron:

$$\Delta H_L(\text{delocalization}) = \tfrac{1}{2}\,\Omega/\gamma_e = \tfrac{1}{2}(\omega_{0c}+\omega_{ex})/\gamma_e . \qquad (7)$$

Again, ΔH_L designates the width of the Lorentzian components of the hyperfine lines. Equation (6) also gives the contribution of the mechanisms of motion considered to the shift of the hyperfine lines. One finds that this contribution is quite negligible.

On the other hand, the effect of these mechanisms on the broadening of the lines is predominant. Figure 4 gives, for one donor concentration, the temperature dependence of the width of the hyperfine lines ΔH. The width of their Lorentzian components ΔH_L is extracted from the experimental width ΔH by the method described in the Appendix and is also plotted in Fig. 4. One sees that ΔH and ΔH_L tend to become equal at high enough temperature. The hyperfine lines are then nearly Lorentzian. It is shown that the temperature dependence of ΔH_L is identical with that of the relative number of electrons in the conduction band,

$$\Delta H_L \propto n_c/(N_D - N_A) \propto e^{-E_0/2k_BT} .$$

This is also observed for all the other samples used. In Fig. 6, we have plotted ΔH_L as a function of the conduction-electron concentration (samples no. 3a, 4, and 6 have been measured at three different temperatures). One observes that over a wide range of donor concentration, ΔH_L is proportional to n_c. According to Eqs. (4), (5), and (7), only the exchange scattering between donor and conduction electrons can give rise to such a concentration dependence. Consequently, the broadening of the hyperfine lines is attributed to this process. We also conclude that the thermal excitation rate to the conduction band ω_{0c} is negligible compared with the exchange rate ω_{ex} and we obtain the following value for the exchange scattering cross section:

$$\sigma_{ex} = 0.35 \times 10^{-12}\ \text{cm}^2 .$$

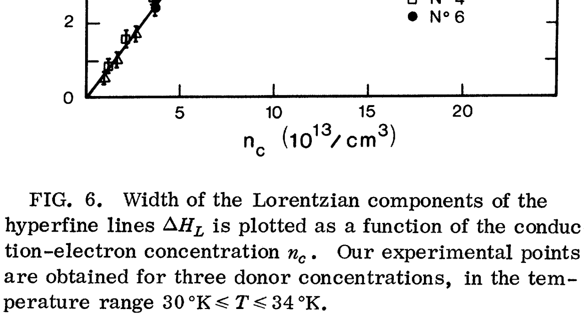

FIG. 6. Width of the Lorentzian components of the hyperfine lines ΔH_L is plotted as a function of the conduction-electron concentration n_c. Our experimental points are obtained for three donor concentrations, in the temperature range $30\,°\text{K} \leq T \leq 34\,°\text{K}$.

This value is in fair agreement with previous experimental estimates.[18]

Summarizing the main results of this section, it is shown that thermal excitation to the first excited level of the donor atom leads to the shift of the hyperfine lines but does not appreciably contribute to their broadening. On the other hand, the broadening is due to the exchange scattering between the donor electrons and the conduction electrons. The detailed study of this effect gives directly the rate of the exchange. No information on the motion of the spins can be obtained from the shift of the lines, since it is a simple effect of the statistical distribution of the electrons between the ground level and the first excited level, and not of their rates of motion between these levels.

V. HYPERFINE STRUCTURE NOT RESOLVED: TEMPERATURE AND CONCENTRATION DEPENDENCE OF LINEWIDTH

A. Narrowing of Line in Low-Temperature Region ($50\,°\text{K} \leq T \leq 75\,°\text{K}$)

The broadening of the hyperfine lines at $T \approx 30\,°\text{K}$ is explained in Sec. IV as an effect of the exchange scattering between bound and conduction electrons. We show in this subsection that the essential feature of the resonance spectrum at slightly higher temperatures (rapid narrowing of the line with increasing temperature) is still due to the same mechanism.

The exchange rate ω_{ex} is proportional to the concentration of the conduction electrons. At the temperatures we now consider, this concentration is high enough for the exchange rate to be larger than the hyperfine interaction ($\omega_{ex} > A$; rapid motion of the spins). Equation (6) shows that it is a sufficient condition for the hyperfine lines to merge into a single central line. The width of this line, Δ_{HF}, is then given by

$$\Delta_{HF} = (1/\gamma_e)[n_0/(N_D - N_A)](A^2/4\Omega) , \tag{8}$$

where Ω is the rate of jumping of the resonance frequency. Neglecting again the rate of excitation to the conduction band with respect to the exchange rate, we may rewrite Eq. (8) as

$$\Delta_{HF} = (1/\gamma_e)[n_0/(N_D - N_A)](A^2/4\sigma_{ex} v n_c) . \tag{9}$$

This contribution to the linewidth due to the averaging of the hyperfine interaction depends on temperature and donor concentration through the relative number of electrons in the ground state $n_0/(N_D - N_A)$ and the conduction-electron concentration n_c. The ratio $n_0/(N_D - N_A)$ increases with the donor concentration but slower than n_c. Thus, it results from Eq. (9) that Δ_{HF} is a smoothly decreasing function of the donor concentration. That is what we actually observe for the experimental linewidth at the lowest limit of the temperature range considered (T

≈ 50 °K). The remarkably large value of the linewidth obtained for the compensated sample no. 3b can be interpreted in the same way. For this sample the ionization of the donor atom is very weak in the temperature region investigated, so that the conduction-electron concentration is very small, while the relative population of the ground level is large.

These two quantities have opposite temperature dependences: n_c increases with temperature while $n_0/(N_D-N_A)$ decreases. As a result, Δ_{HF} is a rapidly decreasing function of the temperature. Actually, the resonance line narrows when the temperature increases in the region of interest. However, for the highest donor concentrations used, the narrowing is not as sharp as predicted by Eq. (9). We shall show that, for these concentrations, we cannot neglect the influence of another relaxation mechanism which is predominant at intermediate temperatures and also significantly contributes to the linewidth in the low-temperature region.

B. Broadening of Line in High-Temperature Region ($150\,°\mathrm{K} \leqslant T \leqslant 300\,°\mathrm{K}$)

We discuss now the behavior of the line in the upper part of the temperature range, in which most of the donor electrons are excited into the conduction band.

Elliott[19] and, more recently, Yafet[20] have calculated the longitudinal spin-relaxation time T_1 of conduction electrons in metals and semiconductors. In the temperature range considered, their results also give the value of the transverse relaxation time T_2, since in that range the correlation time of the fluctuating magnetic interaction responsible for the spin relaxation is certainly short enough to make $T_1 = T_2$.

Elliott's theory is based on the following argument. Since the conduction electrons experience a spin-orbit interaction, they cannot be described by pure spin states but, rather, by admixtures of opposite spin states. Therefore, in a collision in which the electron momentum is changed, the spin orientation also may be changed. As a result, the spin relaxation rate and the momentum-relaxation rate must be correlated, regardless of the collision process involved.

For the collisions on phonons we expect, from the work of Elliott and of Yafet,[21] the spin-relaxation rate $1/T_1$ and the lattice mobility μ_L to be connected by a relation of the type

$$1/T_1 = \lambda T/\mu_L \,, \tag{10}$$

where λ is a constant independent of temperature. The temperature dependence of the lattice mobility is well known from previous measurements.[22] μ_L is approximately described by a power law in $T^{-3/2}$ for $T \lesssim 150$ °K and $T^{-5/2}$ for $T \gtrsim 150$ °K. Thus, it follows from Eq. (10) that the phonon collision process should result in a spin-relaxation rate which increases with temperature as $T^{5/2}$ and $T^{7/2}$ in these two regions, respectively.

Following Elliott,[19] a concentration-dependent spin-relaxation mechanism is associated with the ionized-impurity scattering of the conduction electrons, as the "intrinsic" process previously discussed is associated with the lattice scattering. The spin-relaxation rate due to the ionized impurities is related to the impurity mobility μ_I by an equation similar to Eq. (10), with μ_I substituted for for μ_L. As a result, this rate is an increasing function of the number of ionized donors. At room temperature, ionization of the donors is very nearly complete for all the concentrations used, so that the ionized-impurity concentration is two orders of magnitude larger for the more heavily doped sample no. 6 than for the purest one (sample no. 1). At the same temperature, the linewidth observed for sample no. 6 is only about 10% larger than for sample no. 1. If we attribute this difference to the ionized-impurity scattering, we may conclude that for the purest sample this mechanism is completely negligible at room temperature. Even for the more heavily doped samples, its contribution remains a small correction in the whole temperature and concentration range investigated. We have calculated this contribution using the results of Kodera at higher donor concentrations.[3] These results give the value of the proportionality factor λ which connects the spin-relaxation rate to the impurity mobility μ_I. The variations of μ_I with temperature and concentration are obtained from a theoretical estimate[23] and experimental measurements.[24]

Thus, at high temperatures, the phonon collision process is, by far, predominant for the spin-relaxation. Its contribution, Δ_{Ph}, to the total linewidth is obtained from Eq. (10), in which we add a weighting factor $n_c/(N_D-N_A)$ to take into account the noncomplete ionization of the donor atoms. We choose the value of the constant λ so that at room temperature Δ_{Ph} is equal to the linewidth observed for our purest sample.

C. Minimum of the Linewidth in Intermediate Temperature Region ($75\,°\mathrm{K} \leqslant T \leqslant 150\,°\mathrm{K}$)

Summarizing the results of the previous paragraphs, we see that two relaxation processes are fully effective at the two extreme parts of our temperature range: (i) averaging of the hyperfine interaction in the low-temperature region; (ii) collisions of the free carriers with phonons in the high-temperature region. Since the corresponding contributions to the linewidth have opposite temperature dependences, this width must present a minimum in the intermediate temperature region. From Eqs. (9) and (10) the value of this minimum is expected to be very small and to decrease when the donor concentration increases. This concentration dependence of the minimum is not actually observed, and the value we measure is much larger than predicted.

At intermediate temperatures, the occupation probability of the (1) states presents a large maximum [see Fig. 2(b)]. Therefore, a spin-flipping interaction acting on the electron in these states is expected to result in an effective relaxation mechanism in the intermediate temperature region. We show in this section that the behavior of the linewidth at these temperatures is actually well understood if the magnetic interaction in the intermediate states (1) is taken into account.

As pointed out by Roth,[25] the impurity potential in n-type silicon gives rise to a spin-orbit interaction which partly lifts the degeneracy of the triplet level $1s$-T_2. The eigenstates of this level are then no longer pure spin states but admixtures of opposite spin states. Taking into account the Zeeman and the spin-orbit interaction, Castner[26] has given a detailed calculation of these eigenstates. Figure 7 shows the level scheme obtained to first order in the spin-orbit interaction Λ_{SO}, assuming that Λ_{SO} is smaller than the Zeeman energy H. Castner's notations have been used: T_x, T_y, T_z denote three linear combinations of the $1s$ hydrogenic orbitals associated with each minimum, which transform like x, y, z and form a basis for the T_2 representation of the tetrahedral group; a^+, a^- are coefficients of order unity and b^+, b^-, of order Λ_{SO}/H. As shown by the figure, the resonance spectrum in the $1s - T_2$ level would consist of three lines in the absence of motion of the donor electron. In the level scheme used in the statistical calculation, this motion results from the decay of the electron to the ground state and from its thermal excitation to the conduction band[27]; we denote the rates of these processes by ω_{10}, ω_{1c}, respectively. The sum of these these rates $\omega_{10}+\omega_{1c}$ characterizes the rate of jumping of the resonance frequency from the values associated with the lateral lines to that corresponding to the central line. Using Anderson's theory,[14] one easily shows that the lateral lines cannot be observed if the rate of jumping $\omega_{10}+\omega_{1c}$ is larger than the difference between the resonance frequencies, Λ_{so}. Experiment indicates that we actually are in that case. The width Δ_{SO} of the single central line is then given by

$$\Delta_{SO} = \tfrac{4}{10}\left[n_1/(N_D - N_A)\right]\Lambda_{SO}^2/\gamma_e(\omega_{10}+\omega_{1c}) \ . \quad (11)$$

The transition rates ω_{10} and ω_{1c} concern individual donor atoms, so that they do not depend on the concentration. As the decay rate ω_{10} mainly involves spontaneous phonon emission in the temperature range considered, it may also be taken as temperature independent. On the other hand, the excitation rate ω_{1c} should increase with temperature as e^{-E_1/k_BT}, where E_1 is the ionization energy of the (1) states ($E_1/k_B \approx 380$ °K). According to Eq. (11), the only concentration dependence of the linewidth Δ_{SO} arises from the first factor $\frac{4}{10} n_1/(N_D - N_A)$, which gives the relative occupation of the four (1) states affected by the spin-orbit interaction.

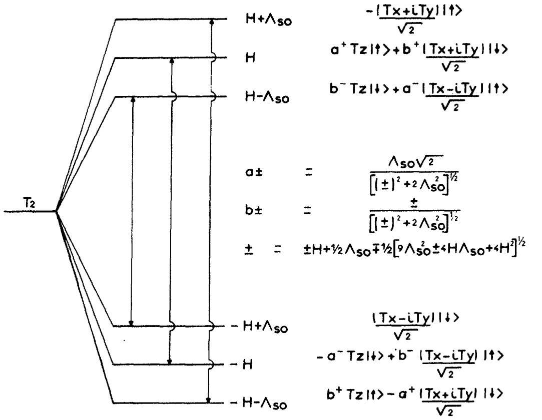

FIG. 7. Energy-level diagram and wave functions obtained for the $1s - T_2$ level of the donor atom when the Zeeman energy H and the spin-orbit interaction Λ_{SO} are taken into account. The level energies are given to first order in Λ_{SO} for $\Lambda_{SO} \ll H$. The direction of the dc magnetic field is along one of the principal axes of the crystal. The arrows indicate those states which are coupled by a transverse magnetic field.

The proportionality of Δ_{SO} to this occupation number is well verified in the intermediate temperature region, as illustrated by Fig. 8 in which we have plotted the ratio $n_1/(N_D - N_A)\,\Delta_{SO}$ as a function of e^{-E_1/k_BT}, for three values of the donor concentration N_D. The value of Δ_{SO} is obtained in this region by subtracting from the experimental linewidth the remaining contributions of the low- and high-temperature processes. Figure 8 shows that the ratio $n_1/(N_D - N_A)\,\Delta_{SO}$ is approximately independent of the donor concentration and that the experimental points for different temperatures fit fairly well on a straight line.

From these results we do not obtain separately the value of the spin-orbit interaction Λ_{SO} and that of the transition rates ω_{10} and ω_{1c}, but only their ratios $\omega_{10}/\Lambda_{SO}^2$ and ω_{10}/ω_{1c}. If one takes the decay rate ω_{10} to be the value given in Ref. 15, one finds for the spin-orbit interaction,

$$\Lambda_{SO} = 1.5\times 10^9 \text{ sec}^{-1} \ .$$

In the same way, we can estimate the average

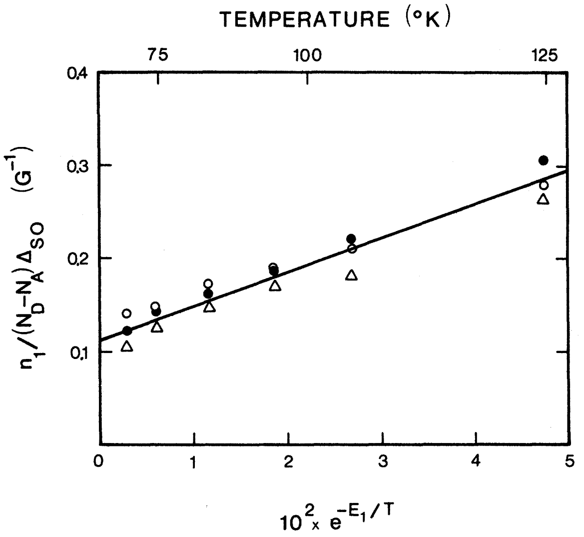

FIG. 8. The ratio between $n_1/(N_D-N_A)$ and Δ_{SO} is plotted as a function of e^{-E_1/k_BT}, where E_1 and $n_1/(N_D-N_A)$ are, respectively, the ionization energy and the relative population of the level (1); Δ_{SO} is the contribution to the total linewidth due to the spin-orbit interaction in this level. The value of Δ_{SO} is obtained by subtracting from the experimental linewidth the calculated contributions of the low- and high-temperature processes.

cross section σ_{c1} of the capture of a conduction electron by an ionized donor in one of the (1) states. The σ_{c1} is obtained from the excitation rate ω_{1c} by the rule of detailed balance:

$$n_1\omega_{1c}=n_c\omega_{c1}=n_c\sigma_{c1}v(n_c+N_A) ,$$

where (n_c+N_A) is the concentration of the ionized trapping centers and ω_{c1} is the rate of the capture on these centers. From our results, we obtain

$$\sigma_{c1}\approx 2\times 10^{-14}\ \text{cm}^2 .$$

VI. COMPARISON WITH EXPERIMENT AND DISCUSSION

In the present work we have been concerned with the detailed study of a mixed electronic system (localized and delocalized electrons) for which spin relaxation occurs through a variety of different processes. The resultant linewidth, which is the sum of the contributions of the different mechanisms, has been calculated with only two adjustable parameters. Its value is plotted in Fig. 9. A comparison of Figs. 9 and 5 shows that the experimental results are well predicted by the theory in the wide temperature and concentration ranges of our experiments.

In these ranges, the electrons are shared between the conduction band and the individual donor levels. Only the ground and the first excited levels can be appreciably occupied and the population of the other ones is negligible at all temperatures. The spin-resonance behavior of the electronic system may then be analyzed in terms of a "three-level" scheme: ground level, intermediate level, and conduction band. The motion of the spins results from the thermally induced transitions between these levels and from the exchange collisions between bound and conduction electrons. This motion modulates the magnetic interactions of the electron in the different states and thus gives rise to spin-relaxation mechanisms.

Table II summarizes the main features of the resonance spectrum in each temperature region and indicates which mechanism is responsible for these features. Of course, there is no clear-cut demarcation between these regions; each of them is characterized by a dominant spin-relaxation mechanism. In the high-temperature region, almost all the donor electrons are excited into the conduction band; then the resonance line obviously behaves as for a conduction-electron system. At low

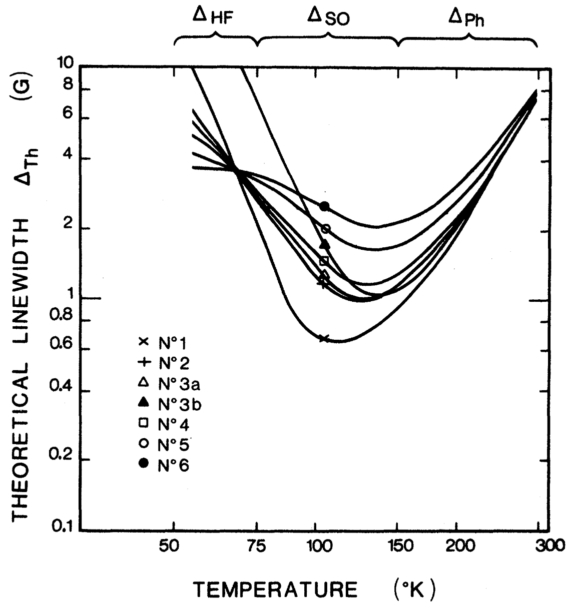

FIG. 9. Temperature dependence of the theoretical linewidth Δ_{Th} resulting from the different relaxation mechanisms studied. For each temperature region the predominant contribution to the linewidth is indicated in the top of the figure. A comparison with Fig. 5 shows a good agreement between the experimental linewidth and the calculated one with two adjustable parameters in the whole range of temperature and concentration investigated.

temperatures, where most of the electrons are trapped in the ground state of the donors, the same mechanism gives rise to two different effects: The motional averaging of the hyperfine interaction through the exchange collisions between donor and conduction electrons gives rise to the broadening of the hyperfine lines at $T \approx 30\,^\circ\mathrm{K}$ and to the narrowing of the single line observed at slightly higher temperatures. Furthermore, we note that we do not find a very narrow resonance line in the intermediate temperature region. At these temperatures, the population of the first excited states is important and the motional averaging of the spin-orbit interaction in these states results in an effective relaxation mechanism. This interaction is relatively small in the case of phosphorus. For arsenic it is one order of magnitude larger. This explains that arsenic-doped silicon gives no detectable signal for concentrations and temperatures comparable with those used in this study.

TABLE II. Summary of the results.

Temperature region		$20\,^\circ\mathrm{K} < T < 40\,^\circ\mathrm{K}$		$50\,^\circ\mathrm{K} < T < 75\,^\circ\mathrm{K}$	$75\,^\circ\mathrm{K} < T < 150\,^\circ\mathrm{K}$	$150\,^\circ\mathrm{K} < T < 300\,^\circ\mathrm{K}$
Main features of the resonance spectrum		Hyperfine structure resolved (2 lines)		Hyperfine structure nonresolved (1 Lorentzian line)		
		Shift of the hyperfine lines	Broadening of the hyperfine lines	Narrowing of the line with increasing temperature	Minimum of the linewidth	Conduction-electron resonance: rapid broadening of the line with increasing temperature
Mechanism responsible	Interaction	Hyperfine interaction	Hyperfine interaction	Hyperfine interaction	Spin-orbit interaction in the first excited level	Impure spin states in the conduction band (Elliott-Yafet)
	Mechanism of modulation of the interaction	Thermal excitation to the first excited level	Exchange between donor and conduction electrons	Exchange between donor and conduction electrons	Excitation to the conduction band. Decay to the ground level	Collision of the conduction electrons on phonons
Temperature dependence of the effect		Shift increasing with temperature as $e^{-\Delta/k_BT}$	Broadening increasing with temperature as the conduction-electron concentration	Strong narrowing of the line with increasing temperature [Eq. (9)]	Minimum of the width weakly dependent on the temperature (like the population of the first excited level)	Width strongly increasing with increasing temperature as $T/\mu_L(T)$
Donor concentration dependence of the effect		Shift independent of the donor concentration	Broadening proportional to the conduction-electron concentration	Weak narrowing of the line with increasing concentration [Eq. (9)]	Width increasing with concentration as the population of the first excited level	Width practically independent of the donor concentration

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APPENDIX

As mentioned in the text, the hyperfine structure lines are Gaussian distributions of Lorentzian lines. Their shape is then described by the following function:

$$I(H)=\int_{-\infty}^{\infty}[(H-t)^2+\Delta H_L^2]^{-1}\frac{e^{-(1/2)\,t^2/\Delta H_G^2}}{\Delta H_G\sqrt{(2\pi)}}\,dt\;,$$

where ΔH_G is the width of the distribution and ΔH_L is the half-width at half-power of the Lorentzian components; H denotes the distance to the resonance field and t is an integration variable. This expression shows that the resonance line is a Gaussian line of width ΔH_G in the limit $\Delta H_G \gg \Delta H_L$ and a Lorentzian line of width ΔH_L in the opposite case. ΔH_G is given by the asymptotic value of our width measurements at low temperature and is also well known from previous experiments[1] ($\Delta H_G = 1.07$ G). We define the experimental width of the hyperfine structure lines ΔH as the peak-to-peak width of the first derivative multiplied by $\frac{1}{2}\sqrt{3}$. This is the half-width at half-power of the line in the Lorentzian limit. We obtain the ratio $\Delta H_L/\Delta H_G$ as a function of $\Delta H/\Delta H_G$ from a numerical computation of the roots of $\partial^2 I/\partial H^2 = 0$.

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[1] G. Feher, Phys. Rev. 114, 1219 (1959).

[2] G. Lancaster, J. A. Van Wik, and E. E. Schneider, Proc. Phys. Soc. (London) 84, 19 (1964).

[3] H. Kodera, J. Phys. Soc. Japan 21, 1040 (1966).

[4] D. Jérome and J. M. Winter, Phys. Rev. 134, A1001 (1964).

[5] S. Maekawa and M. Kinoshita, J. Phys. Soc. Japan 20, 1447 (1965).

[6] W. Kohn, in *Solid State Physics* (Academic, New York, 1957), Vol. 5, pp. 257-320.

[7] T. G. Castner, Phys. Rev. Letters 8, 13 (1962).

[8] D. Long and J. Myers, Phys. Rev. 115, 1119 (1959).

[9] R. L. Aggarwal and A. K. Ramdas, Phys. Rev. 140, 1246 (1965).

[10] C. Y. Cheung and R. Barrie, Can. J. Phys. 45, 1421 (1967).

[11] R. A. Smith, *Semiconductors* (Cambridge U. P., Cambridge, England, 1959); W. Paul, Cours à la Faculté des Sciences de Paris, 1966–1967 (unpublished).

[12] G. K. Walters and T. L. Estle, J. Appl. Phys. 32, 1854 (1961).

[13] S. D. Lacey and G. Lancaster, Phys. Letters 22, 386 (1966).

[14] P. W. Anderson, J. Phys. Soc. Japan 9, 316 (1954).

[15] T. G. Castner [Phys. Rev. 130, 58 (1963)] calculates that the decay rate from the first excited level ω_{10} should be larger than 5.5×10^{9} sec^{-1}. In a recent experimental work, G. Lampel [Thèse de Doctorat d'Etat, Faculté des Sciences de Paris, 1968 (unpublished)] invoked the thermal excitation of the donor electron and the exchange scattering between donor and conduction electrons to explain the spin-lattice relaxation of the Si^{29} nuclei at 77 °K. From his results, one estimates that the decay rate ω_{10} should be of the order of 6×10^{9} sec^{-1}.

[16] Using a reasonable estimate for the decay rate ω_{10} ($\omega_{10}=6\times10^{9}$ sec^{-1}, see Ref. 15), one calculates from Eq. (3) that the contribution of this mechanism to the width ΔH_L is much smaller than that which we actually observe.

[17] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., Oxford, England, 1961), Chap. X.

[18] A value close to 10^{-12} cm^2 has been given for σ_{ex} at liquid-helium temperature by G. Feher and E. A. Gere [Phys. Rev. 114, 1245 (1959)] and R. S. Levitt and A. Honig [J. Phys. Chem. Solids 22, 269 (1961)]. The value determined by G. Lampel (Ref. 15) is, at 77 °K, $\sigma_{\text{ex}}=0.5\times10^{-12}$ cm^2.

[19] R. J. Elliot, Phys. Rev. 96, 266 (1955).

[20] Y. Yafet, in *Solid State Physics* (Academic New York, 1962), Vol. 14, pp. 2–96.

[21] Yafet's calculation (Ref. 20) involves only the scattering of the conduction electrons by the acoustical phonons via normal processes.

[22] The drift mobility measurements performed on pure samples by D. Long and J. Myers [Phys. Rev. 115, 1107 (1959)] in the temperature interval ≈ 30 to ≈ 100 °K and by F. J. Morin and J. P. Maita [Phys. Rev. 96, 28 (1954)] in the interval ≈ 150 to ≈ 300 °K give for μ_L temperature dependences which are close to $T^{-3/2}$ and $T^{-5/2}$ in these temperature regions, respectively.

[23] H. Brooks, Phys. Rev. 83, 879 (1951).

[24] D. Long and J. Myers, Phys. Rev. 115, 1107 (1959).

[25] L. Roth, MIT Lincoln Laboratory Report No. 3, 1962 (unpublished).

[26] T. G. Castner, Phys. Rev. 155, 816 (1967).

[27] Thermal excitation to the upper donor levels (2), (3), etc., can be neglected; since the ionization energy of these levels is less than k_BT in the temperature range considered, we include them in the conduction-band levels.