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Absolute Spin Susceptibilities and Other ESR Parameters of Heavily Doped *n*-Type Silicon. I. Metallic Samples*

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Results are presented for the measured electron spin resonance (ESR) spin susceptibilities of "metallic" phosphorus-doped silicon with $N_D \geq 1\times 10^{19}$ donors/cm^3. These results agree closely for the case of $N_D \gtrsim 4\times 10^{19}$ donors/cm^3 with values calculated on the basis of a "rigid-band" model of noninteracting Pauli electrons. Evidence for a non-Pauli temperature-dependent-susceptibility component was found in the lower portion of our sample-concentration range. Static-susceptibility data are used together with our results to obtain the diamagnetic susceptibility which exhibits a concentration dependence consistent with the predictions of Kjeldaas and Kohn. Measurements of g values and linewidths are presented as evidence for the proposal that the Fermi level enters the host conduction band at a concentration $N_D \approx 2\times 10^{19}$ donors/cm^3. These data are also used to verify Elliot's theory of impurity-scattering spin relaxation and to demonstrate g-value anisotropies characteristic of the silicon conduction band.

I. INTRODUCTION

In a previous publication[1] we have presented relative magnetic-spin-susceptibility data for silicon samples having phosphorus impurity concentrations N_D near to or in excess of $N_D^c \sim 3\times 10^{18}$ donors/cm^3. The critical donor impurity concentration N_D^c has been associated[2] with a semiconductor-metal or "Mott" transition in these materials. Our susceptibility measurements indicated the existence of qualitative differences in the concentration and temperature dependences of samples with concentrations above and below $N_D \sim 10^{19}$ donors/cm^3, respectively. For the purposes of the present discussion and because of the details of these dependences, we have designated these concentration regions as "metallic" and "impurity banded, " respectively. This classification is similar to that previously proposed by Holcomb and Alexander[2] based on the assumption that an "impurity banded" to "metallic" transition occurs when the Fermi energy enters the normal conduction band of the host lattice.

We have now extended our measurement techniques to obtain absolute spin-susceptibility values. This article will outline and briefly discuss these techniques prior to a presentation and discussion of the data for specifically "metallic" samples. It will be seen that the spin susceptibility approaches that of a Pauli electron gas when the donor concentration is above roughly 4×10^{19} donors/cm^3. There is evidence of a non-Pauli-like temperature-dependent susceptibility in the lower portion of our sample-concentration range. Further, diamagnetic susceptibilities, obtained through the use of previous static-field data,[3] exhibit a concentration dependence reasonably consistent with the predictions of the Kjeldaas-Kohn calculation.[4]

In the course of our susceptibility measurements it was possible to accurately measure the linewidths and g values of the observed signals. These data will also be presented and discussed in the light of previous theories and the "rigid-band" model inferred from our susceptibility results.

II. EXPERIMENTAL DETAILS

Our electron spin resonance (ESR) measurements were carried out on powdered silicon samples in a standard x-band microwave spectrometer utilizing phase-sensitive detection relative to a modulated magnetic field. The samples were prepared by mortar and pestle grinding of slices cut from purchased[5] single-crystal boules. Sample concentrations were obtained by four-point-probe resistivity measurements[6] of the slices prior to grinding. The "surface" ESR line produced by the grinding was eliminated by an HF-HNO$_3$ etch and a subsequent heating to 600 °C in air.[7] All powders were separated into portions of relatively uniform powder size. The data to be presented here were obtained through the use of powders having particle sizes ranging from 2 to 5 μ. These particle sizes were small enough to avoid the line-shape distortions discussed by Dyson[8] in connection with the finite electromagnetic field skin depths of conducting samples. Instead, our observed ESR lines were of Lorentzian form and appeared to represent all the spins of each particle. This eliminated the need for the skin-depth corrections necessary in the case of bulk or single-crystal samples.[9] It is also important to note that the sample particle sizes were sufficiently large to avoid the extrinsic effects expected in the case of large surface-to-volume ratios. The presence of such size effects in our data seems unlikely in view of the fact that identical results were obtained with slightly coarser powders.

Our measurements of the spin susceptibility χ_s utilized an expression for this quantity which was first derived by Schumacher and Slichter.[10] This expression describes the proportionality which, in certain cases, exists between χ_s and the integrated value of χ'', the imaginary component of the complex susceptibility $\chi = \chi' - i\chi''$. It is based on the applicability of the Kramers-Kronig relations[11] and can be written as

$$\chi_s = \chi'(0) = (2\gamma/\pi\omega_0) \int_0^\infty \chi''(H)\, dH, \qquad (1)$$

where γ is the spin gyromagnetic ratio and ω_0 is the angular frequency of the monochromatic-microwave spectrometer used to observe $\chi''(H)$ as a function of the magnetic field H. The applicability of Eq. (1) to the case at hand can be justified since the magnitude of the linewidths of the observed ESR lines are always much less than the resonant field value $H_0 = \hbar\omega_0/\gamma$. Further, because of the linear-response assumption fundamental to the Kramers-Kronig result, Eq. (1) is valid only in the absence of saturation. This restriction can easily be satisfied in the present case through the use of sufficiently low microwave power levels.

Inasmuch as the output of our field-modulated spectrometer was proportional to $d\chi''/dH$ an evaluation of Eq. (1) requires a double integration of this signal. This integration of the digital output data was carried out with the aid of an IBM 360 computer.

The main obstacle to the combined use of Eq. (1) and the doubly integrated output data is the mere (spectrometer-dependent) *proportionality* that exists between the output signal and $d\chi''/dH$. As a result, "comparison" methods are generally necessary to obtain the required absolute values of these quantities. These methods[12] effectively evaluate the spectrometer "proportionality factor" by simultaneously or nearly simultaneously observing the signals arising from the sample of interest and from a suitable calibration material of known susceptibility. This comparison has usually been achieved by placing the two samples at adjoining positions in the spectrometer resonant cavity. Obvious difficulties arise with this technique when the linewidths of one or both of these samples become comparable to the separation of their resonant fields. The resulting overlap of the two signals greatly complicates the evaluation of the individual integrated signal outputs. This difficulty has been present in earlier measurements of Si:P susceptibilities[9,13,14] and has only been eliminated in the recent work of Ue and Maekawa[15] and in our own work.[1]

Our measurements were made in three basic steps: (a) a relative-susceptibility comparison of the samples at $T = 1.1$, 4.2, and 77 °K; (b) a correlation of these three sets of isothermal results; and (c) an absolute-susceptibility calibration. These steps will now be described in some detail.

A. Relative Susceptibility Measurements

The measurements consisted of a series of direct isothermal comparisons of the integrated signal intensities arising from each of two samples simultaneously mounted in a rectangular double-sample modulation-switched (DSMS) TE_{105} cavity. This cavity allowed sample access to the equivalent microwave field positions located $\frac{1}{2}$ wavelength above the cavity bottom and at a similar distance below its iris or top face. The "modulation switch" consisted of a movable length of copper tubing whose central axis coincided with the long axis of the cavity and whose vertical position was controlled from the cryostat exterior. This tubing mated snugly with flanges mounted on the outside walls of the cavity so as to allow almost complete attenuation of the modulated portion of the magnetic field at either of the two sample sites. This attenuation was due to the fact that the wall thickness of this tubing was much greater than the skin depth at the magnetic-field-modulation frequency. Inasmuch as the ESR signals arising from the two sample sites, U and L for upper and lower, respectively, were proportional to the modulation fields at these sites, this tubing "switch" could "turn off" either of these signals without affecting the other or "on" signal. This switching is illustrated in Fig. 1 and required no changes in the microwave or electronic detection systems. It allowed a simple and accurate determination of relative signal intensities even in the presence of large signal overlap.

Our powder[16] samples were confined in almost identically machined capped Lucite tubes which fitted tightly into Lucite holders which were rigidly attached to the cavity walls near each sample site. For a given pair of samples the switch was manipulated to successively give the upper-sample signal (S_U), lower-sample signal (S_L), and the completely

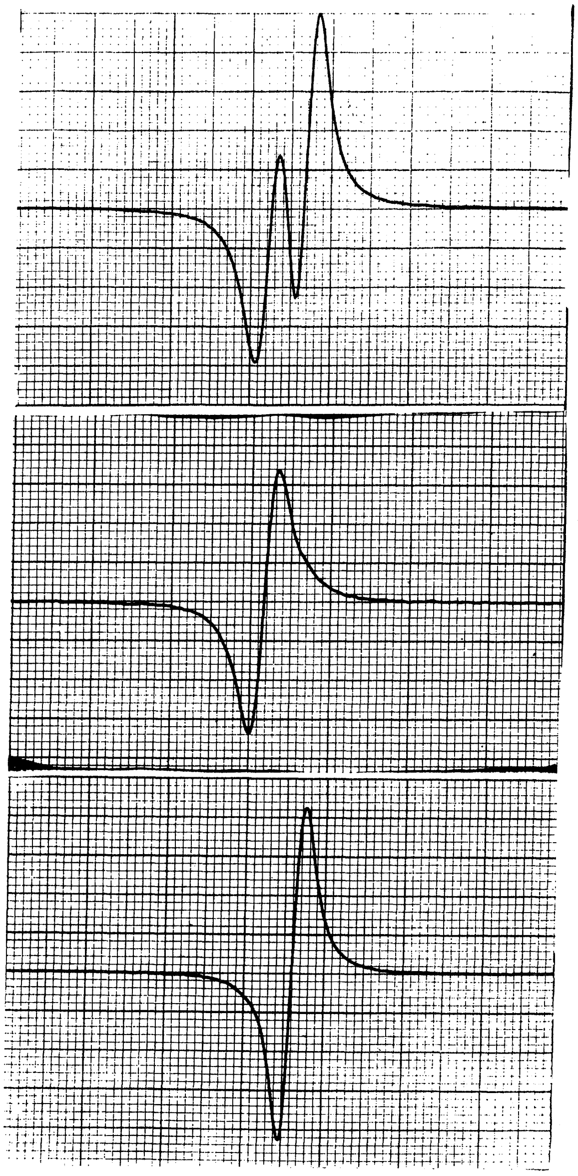

FIG. 1. Typical experimental spectra observed with DSMS cavity, upper trace: both samples unshielded; middle trace: upper sample shielded; lower trace: bottom sample shielded.

unattenuated signal $(S_U + S_L)$. Digital $d\chi''/dH$ data were taken and a similar run was performed in which the positions of the two samples were interchanged. This last step was necessary to account for any inequivalence in the two sample sites. A susceptibility comparison of any such pair of samples required the integrated signal intensities obtained in any two switch configurations. However these quantities were measured in all three switch configurations as a consistency check. We estimate that this procedure gives the susceptibility ratio of any pair of samples of similar composition (see below) to within 3%.[17] This error has been equated to the maximum deviation observed between measured weight and susceptibility ratios for a pair of samples prepared from the same powder portion.

Our procedure then involved comparing sample pairs in a consistent manner to obtain a susceptibility-vs-concentration curve relative to the arbitrary standard of our reference sample. A more complex intercomparison scheme than that previously reported[1] was used to minimize the possibility of pyramiding errors. These measurements were performed at 1.1, 4.2, and 77 °K.

B. Relative Temperature Dependence

The three isothermal curves were related to each other by susceptibility comparisons (again using the DSMS cavity) of a Si: P sample and a sample of known temperature dependence.

The primary standard used in these comparisons was a small piece of annealed neutron-irradiated LiF[18] (LiF: Li). The narrow ESR line characteristic of this material[19] originates from small globules of lithium metal, which has been shown to have the temperature-independent spin susceptibility expected of a degenerate electron gas.[20] The DSMS comparisons were performed at sufficiently low microwave power to avoid saturation and nuclear-polarization effects[21] in the LiF: Li.

Additional comparisons were made using polycrystalline diphenylpicrylhydrazyl (DPPH) and single crystal $CuSO_4 \cdot 5H_2O$ as standards. Results calculated from these measurements, using the known Curie-Weiss behavior[22,23] of these materials, agreed well with those previously obtained with LiF: Li.

This information then allowed the positioning on the same diagram of the three isothermal relative susceptibility-vs-concentration curves. Such a diagram has been presented in Ref. 1 expressing the susceptibilities of several samples at all three temperatures relative to that of a $N_D = 2.5 \times 10^{18}$ donors/cm^3 sample at $T = 1.1$ °K.

C. Absolute Susceptibility Calibrations

Although the absolute susceptibility of metallic lithium has been accurately measured,[10,20] the difficulties involved in estimating the amount of this metal in our LiF: Li samples precluded their use as absolute standards. Instead we found that accurate and consistent calibration could be obtained with the more common DPPH and $CuSO_4 \cdot 5H_2O$ standards if certain precautions were taken. The most obvious of these precautions must account for the fact that neither of these materials follows the simple Curie law in the liquid-helium-temperature range. The deviations from this law apparently have not always been recognized in previous calibrations.[24,25] We at first avoided this difficulty by calibrating against these standards at 77 °K where the Curie law deviations have negligible effect. These results were consistent with those later obtained by calibrations against these standards at 4.2 °K in which the correct Curie-Weiss susceptibility expressions[22,23] were used.

A more serious error could be introduced by differences in the microwave field intensity at the Si:P and "standard" sample sites. These differences might arise from the different microwave field enhancements expected because of inequalities in the dielectric coefficients of Si:P and the "standard" material. Fortuitously the $CuSO_4 \cdot 5H_2O$ dielectric coefficient is nearly equal to that calculated for the silicon powder mixtures which constitute our samples, thus minimizing enhancement errors in this case. Nevertheless, variations in the packing density of the Si:P samples resulted in observable but small changes in the measured susceptibilities consistent with the corresponding changes in the dielectric coefficients.

The main difficulty with DPPH standards arises from the sensitivity of the observed ESR intensity to the exact positioning of these "point" samples. We minimized both this effect and any Si:P—"standard" dielectric mismatch by breaking up and dispersing the DPPH crystals in a matrix of intrinsic silicon powder.[26] The main source of error in our DPPH calibration appeared to be the limited knowledge of this material's spin density and low-temperature behavior as well as the possibility of a spin-density reduction due to the increased surface area of the "broken-up" sample.[12]

Inasmuch as a significant portion of the discussion in Sec. III will be concerned with relatively fine features of the experimental data, it is appropriate at this point to clearly specify the estimated accuracy of our measurements. It is particularly important to distinguish between the "relative" and "absolute" portions of our procedure. Thus because of both the sensitivity of the DSMS technique and the availability of consistency cross checks through the use of different sample pairings, it was possible to specify the relative susceptibility of any two samples at the same temperature to within 3%. However this accuracy was not obtainable in our temperature-dependence or absolute-value determinations. Instead dielectric mismatches, spin-density uncertainties and (in the case of LiF:Li) remanent saturation and nuclear polarization limited our specification of absolute values and single-sample ratios such as $\chi_s(4.2\,°\mathrm{K})/\chi_s(1.1\,°\mathrm{K})$ to within about 7%. This last estimate seems reasonable since our results obtained with each of the three standards agreed to within this figure and there seems to be little likelihood of other unaccounted systematic errors. Thus, although single-temperature and single-sample susceptibility ratios may be specified to a slightly greater accuracy, error bars of ± 10% seem appropriate for our absolute susceptibility data plotted as a function of temperature and concentration.

III. SUSCEPTIBILITY RESULTS AND DISCUSSION

The data points plotted in Fig. 2 represent measured values of the spin susceptibility χ_s as a function of concentration at the temperatures 1.1, 4.2, and 77 °K. The curves in this figure represent the susceptibilities per unit mass expected on the basis of a "rigid-band" model in which all unpaired donor electrons exist in host conduction-band states describable by a Pauli susceptibility expression.[27] This expression applied to a degenerate gas of N_D electrons, of effective mass m^*, per unit volume can be written as

$$\chi_s = \frac{\mu_B^2 N_D}{\rho k T} \, \frac{F'_{1/2}(\epsilon_F/kT)}{F_{1/2}(\epsilon_F/kT)}, \tag{2}$$

where μ_B is the Bohr magneton; ρ is the density of silicon; and $F_{1/2}(\epsilon_F/kT)$ and $F'_{1/2}(\epsilon_F/kT)$ represent, respectively, the Fermi integral and its derivative, with the Fermi energy given by ϵ_F. We have evaluated this expression in Fig. 2 for $m^* = 1.03 m_0$, where m_0 is the free-electron mass. This value was chosen to optimize the fitting to our higher-concentration sample data where the Pauli expression is expected[2] to be most appropriate. It is slightly smaller than the density-of-states effective mass[28] $m^* = 1.08 m_0$ obtained from cyclotron-resonance values[29] for the principal components of the effective-mass tensor at the conduction-band minima.

It is seen from the above figure that the Pauli expression closely approximates the data over most of the "metallic" concentration range. In particular, our data show little evidence for the sizably exchange-enhanced susceptibilities deduced from previous static and ESR measurements[3,9,13,15] in similar samples. We feel that this disagreement with earlier work is primarily due to the greater accuracy of our measurements as well as to the incorrect assumption of Landau-Peierls diamagnetism in previous interpretations of the static-susceptibility data[3] (see discussion below). The observed absence of a significant exchange enhancement is to be expected from the small size of the electron-electron interaction relative to the Fermi energy because of the low effective masses and high dielectric coefficients characteristic of this material.[30]

Although the experimental data are in rough agreement with the calculated curves, slightly closer examination indicates the existence of small

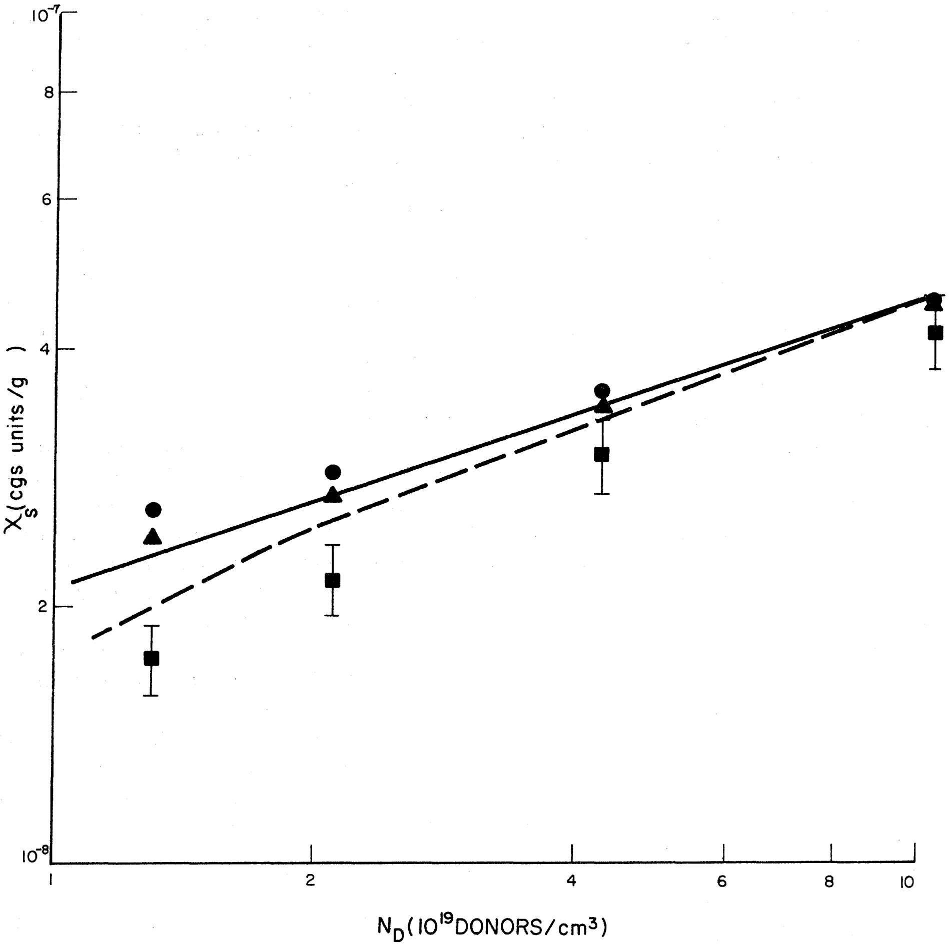

FIG. 2. Spin susceptibility per unit mass χ_s as a function of the donor concentration N_D at $T = 1.1$ °K (circle), $T = 4.2$ °K (triangle), and $T = 77$ °K (square). The solid and broken curves, respectively, represent the "rigid-band" Pauli susceptibility at 1.1 and 77 °K, when $m^* = 1.03m_0$.

but significant deviations from Pauli-like behavior. These deviations are just within experimental error for our two most concentrated (4.3×10^{19} donors/cm^3 and 1.05×10^{20} donors/cm^3) samples but lie outside these limits for the two more dilute samples. Furthermore the signs of the deviations at each temperature are independent of concentration and are consistent with the existence of a non-Pauli susceptibility contribution which follows a roughly Curie-Weiss-type law. This latter behavior characterizes[1] more dilute or "impurity-banded" samples and will be discussed in more detail in a later publication. At the moment however the relevant point lies in the decreasing importance, in our χ_s data, of this non-Pauli component as the sample concentration is increased. Thus this contribution is either absent or too small to be distinguished when $N_D \gtrsim 4 \times 10^{19}$ atoms/cm^3. These results correspond very well with the Si^{29} Knight-shift data of Sundfors and Holcomb[31] which exhibited the Pauli-like $N_D^{1/3}$ dependence when $N_D > 4.5 \times 10^{19}$ donors/cm^3 and a relatively steep falloff from this behavior at lower concentrations. Unfortunately, since their measurements included no samples between $N_D = 4.5 \times 10^{19}$ donors/cm^3 and $N_D = 1.8 \times 10^{19}$ donors/cm^3, Sundfors and Holcomb were not able to precisely determine the concentration at which significant deviations from the $N_D^{1/3}$ law appeared. It is primarily on the basis of this data that Holcomb and Alexander made their proposal[2,32] that the Fermi level enters the host conduction band at the critical concentration $N_D^b \sim 2 \times 10^{19}$ donors/cm^3. The combined use of our χ_s data and interpolations of the Knight-shift results[2] indicates that a rather drastic change occurs in the electronic density at the Si^{29} sites when the donor concentration drops somewhere below $N_D = 4 \times 10^{19}$ donors/cm^3. However the critical concentration N_D^b can be perhaps best inferred from the resulting changes produced in other experimental quantities such as the mobility, magnetoresistance,[2] ESR linewidth, and g values (see Sec. IV). It is important to note that such a transition at $N_D = N_D^b = 2 \times 10^{19}$ donors/cm^3 is not inconsistent with the experimentally observed transition to Pauli-like behavior near $N_D = 4 \times 10^{19}$ donors/cm^3, since a Fermi level in the conduction band does not preclude the existence of "impurity-banded" or perhaps "localized" states at energies below or near the bottom of this band[33] which contribute a non-Pauli component to the observed magnetic behavior. Only when N_D is increased above roughly 4×10^{19} donors/cm^3 will the density of these states become sufficiently small relative to the number of occupied conduction-band states to allow the resultant magnetic properties to approach Pauli-like behavior. However because of the accuracy limits of our techniques it is not possible to positively demonstrate the absence of "impurity-banded" or "non-Pauli" electrons even in our most concentrated samples. Instead we must be content with the conclusion that any such electrons make an almost negligible contribution to most magnetic properties of samples where $N_D > 4\times10^{19}$ donors/cm^3. This however still leaves open the possibility[34] that even a relatively low density of such electrons could be responsible for observed[2,35] negative magnetoresistivities.

We would now like to utilize the above spin-susceptibility data to extract the corresponding diamagnetic susceptibility χ_d results from the extensive static measurements of Sasaki and Kinoshita.[3] In the low-field limit, the static susceptibility may be written as

$$\chi_{\text{static}} = \chi_s + \chi_d \ . \tag{3}$$

We further consider only those experimental values of χ_{static} which have been "corrected" by a subtraction[36] of the "core" susceptibility intrinsic to the silicon host. The resulting susceptibility is then, within the limitations of this procedure, representative solely of the "extrinsic" magnetism contributed by the phosphorus impurities.

We have plotted in Fig. 3 the values obtained at 4.2 and 77 °K for χ_d through the use of Eq. (3) and the static- and spin-susceptibility data. This figure also contains curves representing the corresponding values for the diamagnetic susceptibility expected on the basis of the Landau-Peierls expression[27]:

$$\chi_{\text{LP}} = -\langle f^2\rangle \left(\frac{\mu_B^2}{3\rho kT}\right) N_D \frac{F'_{1/2}\,(\epsilon_F/kT)}{F_{1/2}\,(\epsilon_F/kT)} \ , \tag{4}$$

as applied to our simple "rigid-band" model. The factor $\langle f^2\rangle$ contains[37] the structural details of the host conduction band and can be written as

$$\langle f^2\rangle = m_0^2 \left(\frac{2m_t + m_l}{2m_t^2\, m_l}\right) . \tag{5}$$

In this expression m_l and m_t represent, respectively, the longitudinal and transverse effective masses at the conduction-band minimum. Using cyclotron-resonance data[29] we find $\langle f^2\rangle = 12.8$. The experimentally obtained values for χ_d fall well below the predicted Landau-Peierls results. This disagreement would account for the spin-susceptibility enhancements inferred by Sasaki and Kinoshita[3] on the basis of static data and an assumed Landau-Peierls diamagnetism. The deviation between our experimental and predicted results is not surprising in that even in a pure metal the Landau-Peierls term is but one component of the diamagnetism.[27] In Si:P one would expect additional complications arising from the absence of complete periodicity and the observed[31] conduction-electron "pileup" near the phosphorus impurity sites. It is important to note that the discrepancy from Landau-Peierls diamagnetism $\Delta\chi_{\text{LP}} \equiv \chi_d - \chi_{\text{LP}}$ is not independent of concentration as was the case in the n-type germanium results of Bowers.[36] Figure 4 represents our values for $\Delta\chi_{\text{LP}}$ plotted as a function of donor concentration N_D at 4.2 and 77 °K. The concentration dependence of this quantity in both cases appears slightly greater than $N_D^{1/2}$. Considering the experimental error possibilities and our neglect of the non-Pauli magnetism component observed at lower concentrations, this dependence is reasonably close to the $N_D^{2/3}$ behavior predicted on the basis of a calculation by Kjeldaas and Kohn.[4] In their calculation these authors obtain an expression for the diamagnetic susceptibility of Bloch electrons in terms of the magnitude of the wave vector k_0 at the "spherical" Fermi surface. The first two terms of their result can be written as

$$\begin{aligned}\chi_d &= \chi_{\text{LP}}\left[1 + C_2 (m^*/m_0)\, k_0^2\right] \\ &= \chi_{\text{LP}}\left[1 + C_2 (3\pi^2)^{2/3} (m^*/m_0)\, N_D^{2/3}\right],\end{aligned} \tag{6}$$

where, on the basis of our simple model, we have set $k_0 = (3\pi^2 N_d)^{1/3}$. The second term of this expression should represent the Kjeldaas-Kohn predicted value of $\Delta\chi_{\text{LP}}$. These authors obtained expressions for the coefficient C_2 in terms of both the energy differences and momentum matrix elements between the entire set of Bloch waves at $k=0$ and in terms of integrals involving the functions[38] which occur in a power-series expansion of the band Bloch state. Although the coefficient C_2 has been evaluated[4] for Li and Na we did not attempt such a calculation for the silicon case. This would require a generalization of the Kjeldaas-Kohn C_2 expression to the many-valley conduction-band case as well as detailed cellular wave functions. Such an explicit calculation would be required to check the reasonableness of our experimentally determined value $C_2 = -8.5\times10^{-15}$ cm^2. The observed fractional correction $\Delta\chi_{\text{LP}}/\chi_{\text{LP}}$ has the same sign and a similar magnitude to the result calculated for metallic lithium.

IV. LINEWIDTH AND g-VALUE MEASUREMENTS

The signal observed in our experiments was the derivative of the ESR absorption line. The peak-to-peak width ΔH_{pp} of this signal was measured for

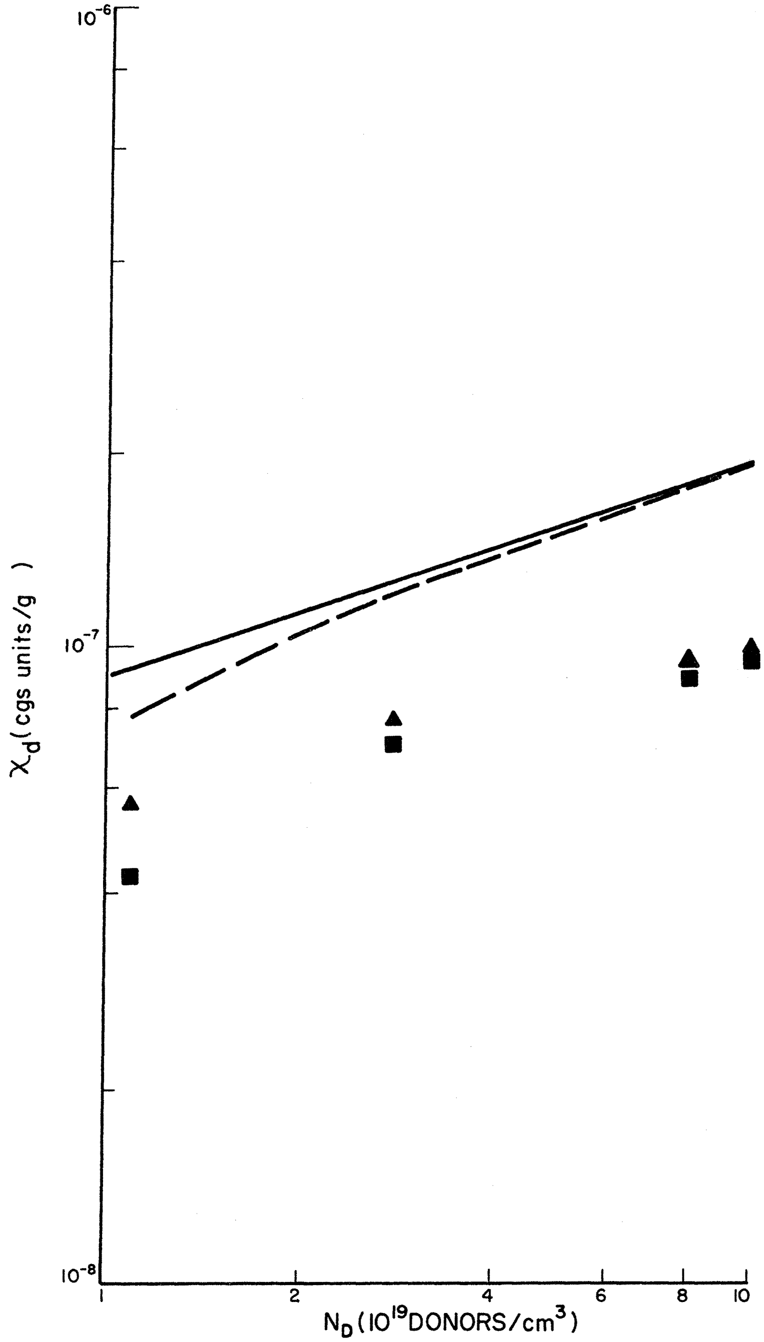

FIG. 3. Diamagnetic susceptibility χ_d as a function of the donor concentration N_D at 4.2 °K (triangle) and 77 °K (square). The solid and dashed curves represent the "rigid-band" Landau-Peierls susceptibility at 4.2 and 77 °K, respectively.

each of the samples at 77, 4.2, and 1.1 °K using a proton NMR to calibrate the magnetic field.

The DSMS cavity was used in measuring the g values associated with the ESR spectra of our samples. Shims on the magnet pole tips were adjusted to give a small field difference (reproducible to ±0.05 Oe) between the two sample sites in order to reduce the overlap of the two signals. The known line shape (which was experimentally verified to be Lorentzian), the previously measured ΔH_{pp}, and the height of each signal (measured using the DSMS cavity) were then used to accurately calculate the field difference between the signals for each pair of samples. Deviations from the known magnetic field difference between the sample sites could then be interpreted as arising from differences in g values. As in the susceptibility work, these measurements were made in pairs, with the samples reversed in the second case. Relative g values were obtained by an intercomparison of the Si:P sam-

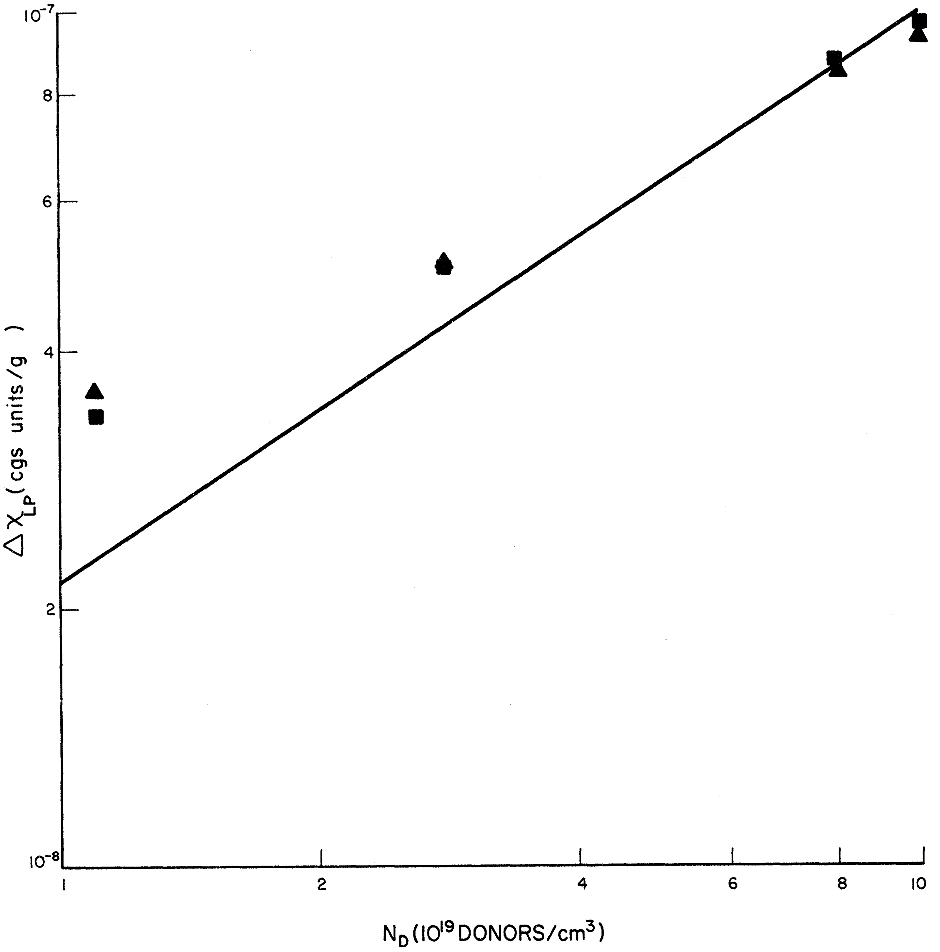

FIG. 4. Landau-Peierls discrepancy $\Delta\chi_{LP} = \chi_d - \chi_{LP}$ as a function of donor concentration N_D at $T = 4.2$ °K (triangle) and $T = 77$ °K (square). The straight line in this figure is illustrative of the $\Delta\chi_{LP} \propto N_D^{2/3}$ behavior expected from a simple application of the results of Ref. 4.

ples, and an absolute calibration was obtained with DPPH ($g = 2.0036$) and LiF:Li ($g = 2.0023$)[7] standards. Proton NMR markers were used to calibrate the magnetic field sweep for all these measurements. Our results are presented in Figs. 5 and 6.

Data[39] on "impurity-banded" samples ($N_D < 10^{19}$ donors/cm^3) are included in these figures in order to emphasize the important changes which occur when the concentration rises above $N_D \sim 2 \times 10^{19}$ donors/cm^3. This transition is sharpest in the g-value data which exhibit an extremely weak concentration dependence in the "impurity-banded" region. The sharp dependence which develops near $N_D = 2 \times 10^{19}$ donors/cm^3 seems indicative of a significant change in the nature of the electrons responsible for the resonance signal. This would be consistent with the proposal[2,32] that the Fermi level enters the host conduction band at this concentration. A similarly sharp change occurs in the concentration dependence of the linewidth at 77 °K. This transition in linewidth behavior is however extended down to lower concentrations at liquid-helium temperatures.

In all cases the linewidth decreases as the temperature is lowered from 77 to 4.2 °K. Upon a further lowering to 1.1 °K, this parameter either increases again or remains unchanged depending upon whether the sample lies in the "impurity-banded" or "metallic" concentration range, respectively. Second, the linewidth is approximately linearly proportional to N_D for $N_D \gtrsim 2 \times 10^{19}$ donors/cm^3.

It is common in conduction-electron spin-resonance work to relate the spin-lattice relaxation time T_1 and the ESR linewidth ΔH_{pp} by the expression

$$\Delta H_{pp} = A/\gamma T_1 , \quad (7)$$

where A is a numerical factor on the order of one which is characteristic of the signal line shape. We shall, for the moment, assume the validity of this expression in order to relate the data of Figs. 5 and 6 to the spin-lattice relaxation processes operative in our "metallic" samples. In this case the resultant proportionality $1/T_1 \propto N_D$ inferred from

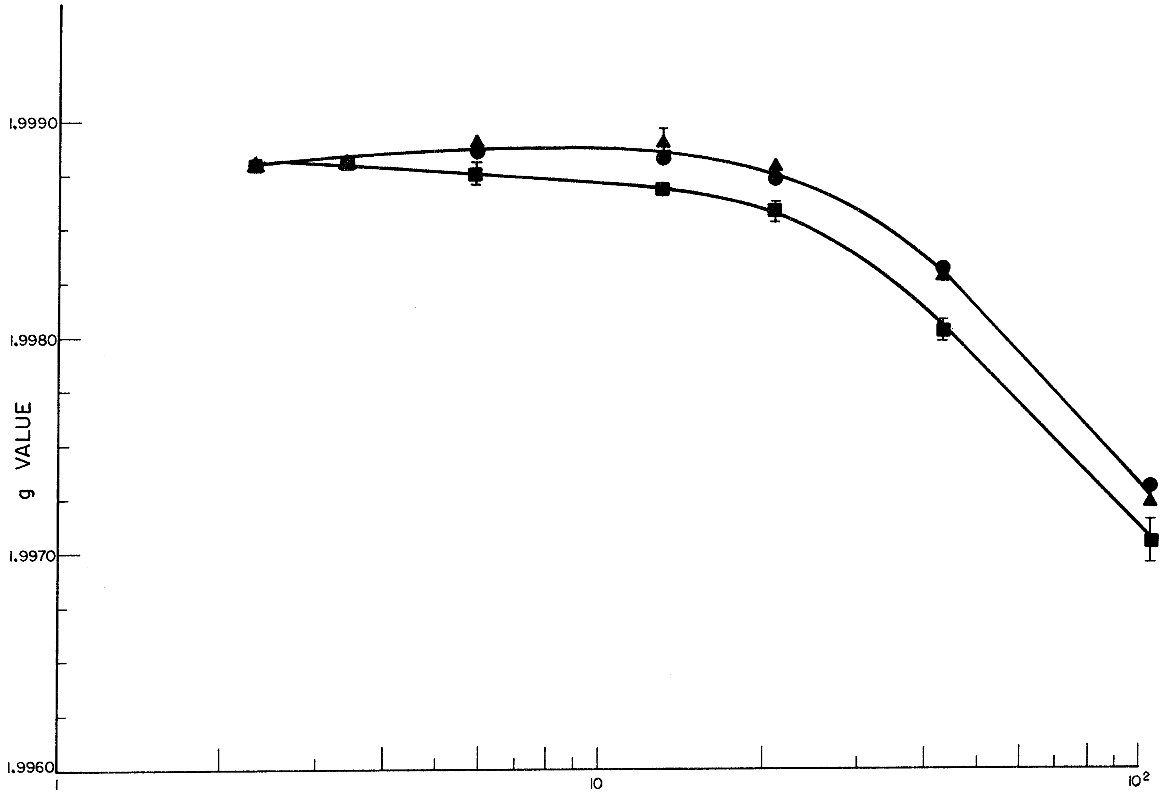

FIG. 5. Experimental g values as a function of the donor concentration N_D at $T = 1.1$ °K (circle), $T = 4.2$ °K (triangle), and $T = 77$ °K (square).

Fig. 6 implies that the donor impurities in these samples provide the dominant spin-lattice-relaxation mechanism for temperatures at least as high as 77 °K. Such extrinsic processes are expected to dominate at low temperatures where intrinsic or phonon-type processes are frozen out. Elliot[40] and Yafet[41] have shown that both impurity- and phonon-type spin-relaxation processes are coupled to the electronic momentum relaxation through the spin-orbit interaction which mixes a component of opposite spin into each unperturbed conduction-band state. Since the shift Δg of the conduction-band g value from that of the free electron is also proportional to this interaction, T_1 can be expressed in terms of the momentum-relaxation time τ_c:

$$T_1 \propto \tau_c/(\Delta g)^2 . \qquad (8)$$

This proportionality is only slightly modified[40] when applied to the case of present interest, namely, the scattering of degenerate electrons by impurities:

$$T_1 \propto \tau_c/N_D^{2/3}(\Delta g)^2 \propto \mu/N_D^{2/3}(\Delta g)^2 . \qquad (9)$$

In Eq. (9) we have utilized the linear relationship between τ_c and the electronic mobility μ. In order to obtain an experimental comparison with this proportionality we have plotted our measured values of ΔH_{pp} as a function of $\delta \equiv N_D^{2/3}(\Delta g)^2/\mu$ in Fig. 7. In plotting our 4.2 and 77 °K data we have obtained the appropriate mobility values from the conductivity and Hall coefficient results of Yamanouchi *et al.*[35] The large horizontal error bars on the experimental points reflect the large scatter in the reported conductivities as a function of concentration. Nevertheless it can be seen that the relationships between ΔH_{pp} and δ are nearly identical at the two temperatures 4.2 and 77 °K. This fact together with the rough linearity of this relationship would seem indicative of the dominance of Elliot's impurity-scattering mechanism for these temperatures. Furthermore, if we use Elliot's rough estimate[40] of the proportionality factor appropriate to (9), the resultant relaxation times agree to within an order of magnitude with those inferred from our linewidth data.

The relatively small deviations of the experimental data of Fig. 7 from the predicted linear relation (9) are not surprising in view of our picture of the electronic states in "metallic" samples. Thus if the bulk of the resonant electrons exist in host conduction-band states, one would expect the result-

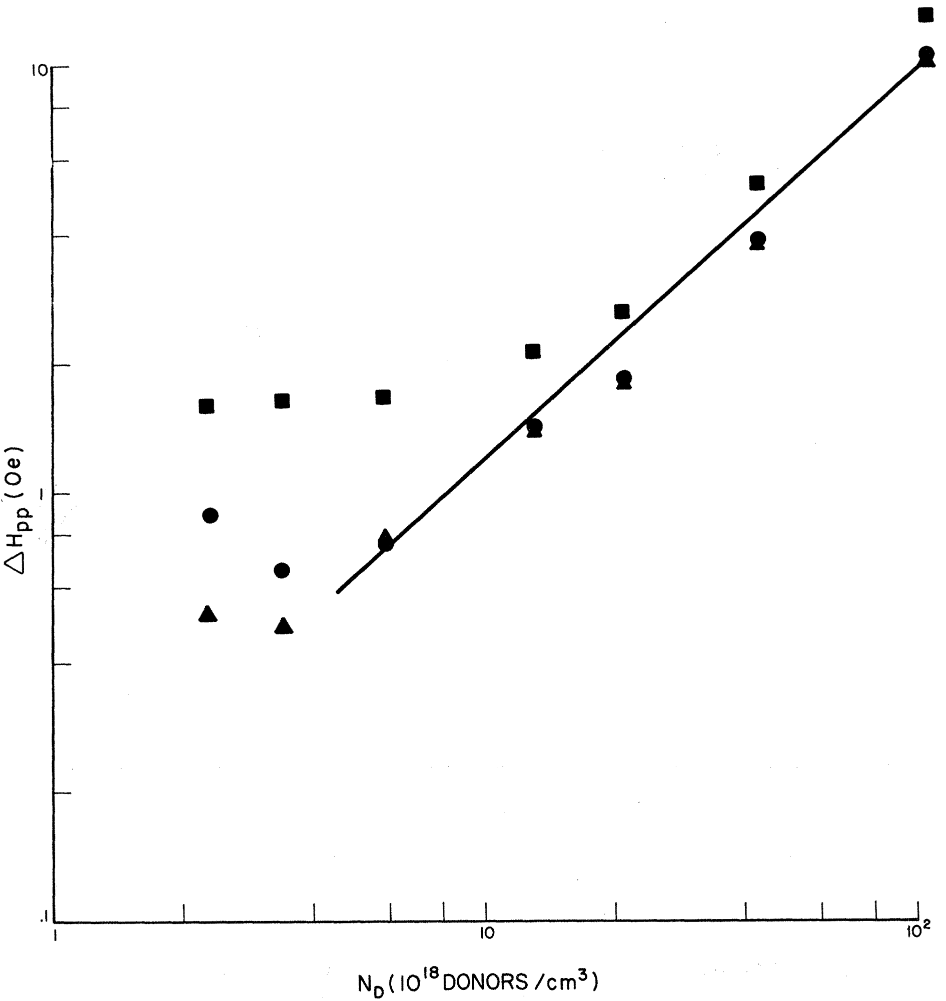

FIG. 6. Measured peak-to-peak linewidths ΔH_{pp} as a function of the donor concentration N_D at $T = 1.1$ °K (circle), $T = 4.2$ °K (triangle), and $T = 77$ °K (square). The straight line in this figure is illustrative of a linear proportionality between ΔH_{pp} and N_D.

ing ESR signal to exhibit evidence of the g-value anisotropies associated with these bands.[41]

In the absence of significant intervalley scattering, one would expect the resultant line shape for a powder sample to be derivable[42] from a convolution of an asymmetric envelope function with the usual Lorentzian line shape. Because the anisotropy in the silicon case is small when compared to the Lorentzian linewidths one would not expect to experimentally observe large deviations from Lorentzian line shapes. This expectation was borne out by the results of a line-shape calculation for a silicon-powder sample which assumed the principle values of the axially symmetric g tensor to be $g_l = 1.9995$ and $g_t = 1.9983$ with "true" Lorentzian linewidths independent of particle orientation with respect to the magnetic field. At $H_0 = 3300$ Oe, assuming "true" linewidths to be those recorded in Fig. 6, the main effects of the anisotropy were (i) to increase the resultant linewidth over the "true" value by an amount which ranged from 0.25 Oe at $N_D = 1.3 \times 10^{19}$ donors/cm^3 to 0.15 Oe for the $N_D = 1.05 \times 10^{20}$ donors/cm^3 sample and (ii) to leave the slightly asymmetric but nearly Lorentzian line centered at a field corresponding to an effective g value $\bar{g} = \frac{1}{3}(g_l + 2g_t)$. The asymmetry of course decreased with increasing linewidth and hence concentration. A more complete calculation, which was not performed, would include the dependence of the linewidth on particle orientation in accord with the Elliot relation (9) and would be expected to further reduce asymmetry because of the preferential broadening of the weighted $g \approx g_t$ contributions. Inclusion of this orientational dependence might also be expected to increase the anisotropy linewidth contribution above that calculated on the basis of our simple model.

In order to verify the importance of anisotropy, we looked for a field dependence of our measured linewidths. Such a dependence would be expected inasmuch as the relative separations of the various component lines should be proportional to the resonant field H_0 (i.e., the most widely split components should be separated by a field $\approx H_0 | g_t - g_l | / \bar{g}$).

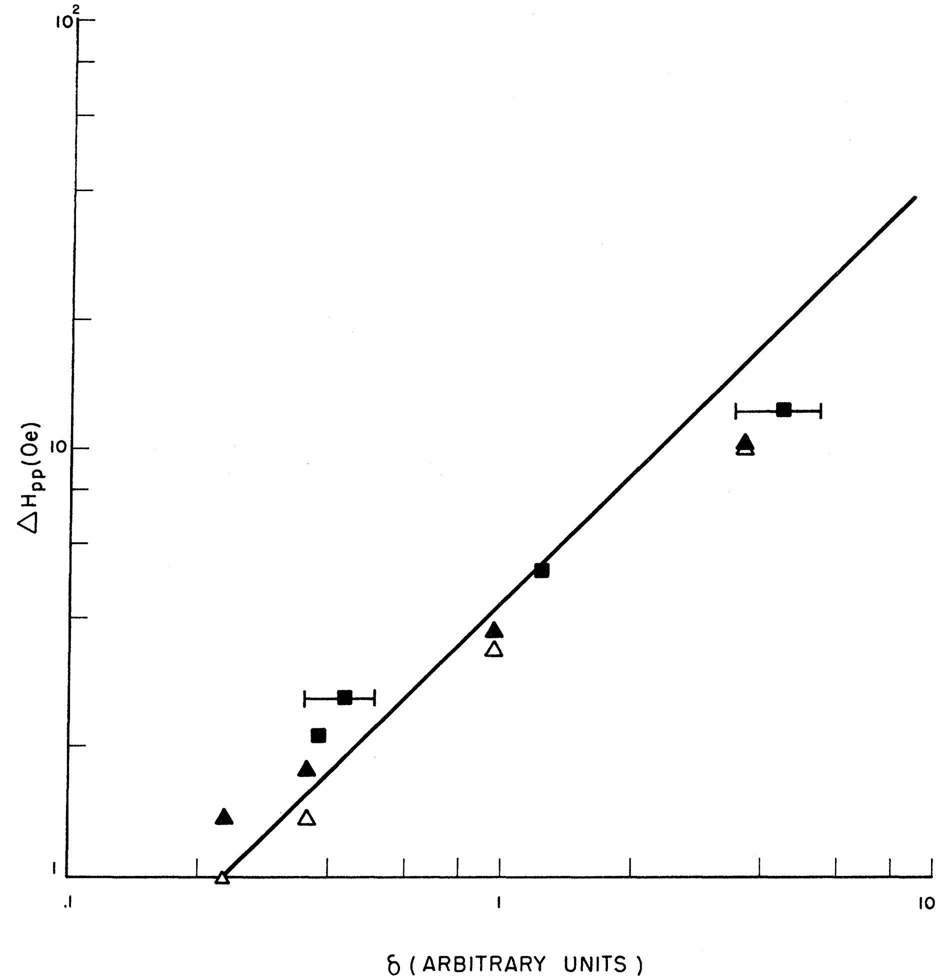

FIG. 7. Peak-to-peak linewidths ΔH_{pp} as a function of the quantity δ defined in the text. Data are plotted for the temperatures 4.2 °K (closed triangle) and 77 °K (square). The open triangles represent 4.2 °K data which have been corrected for the anisotropy linewidth component (see text). The solid line in this figure is illustrative of the proportionality $\Delta H_{pp} \propto \delta$ predicted by the Elliot theory (Ref. 40).

Ue and Maekawa[15] have recently reported data for a 1.6×10^{19} donors/cm^3 sample which indicated an ≈ 0.4 Oe increase in linewidth upon raising the resonant field from ≈ 700 Oe to the 3.3-kOe value associated with *x*-band resonance measurements. The linewidth increment was constant over the 1.5–77 °K range of their experiments. Our own measurements on a 35-GHz spectrometer, at a resonant field of 12.5 kOe gave values of ΔH_{pp} for all "metallic" samples which were approximately 1.5 Oe greater than those obtained at a resonant field of 3.3 kOe.

These results, when combined, suggest the approximate representation of this effect by the addition to the right-hand side of Eq. (7) of an anisotropic broadening term linear in the magnetic field. Such a term would have a magnitude ≈ 0.4 Oe at a resonant field of 3.3 kOe. Such a simple interpretation neglects any field dependence of the spin relaxation, an assumption which will break down at high magnetic fields. Further, our simple linewidth calculation showed increasing line-shape anisotropy and nonlinearity in the field dependence of the anisotropy linewidth contribution as it approaches the relaxation width. A precise extraction of the true relaxation width would require more extensive experimental data. However, our treatment of the problem by the addition to Eq. (7) of a term linear in H_0 seems to be a reasonable first step in such a separation. The "relaxation linewidths" could then be obtained by subtracting the 0.4-Oe anisotropy contribution from the values of ΔH_{pp} measured at 3.3 kOe. For illustrative purposes, these results have been plotted (open triangles) in Fig. 7 for the 4.2 °K data.

This correction steepens the experimental curve, bringing it closer to the linear relationship predicted by Eq. (9). However, one must not make too much of this matching with the Elliot theory, because our powder sample results unavoidably must deal with "average" *g* values and linewidths. Some of the details necessary for a thorough check with the theory are buried in these composite quantities. These details should be observable in a careful study of single-crystal samples. The very small sample thickness required to avoid the complications introduced by Dysonian line shapes[8] make these measurements rather difficult. It has been possible however to verify the existence of a g-value anisotropy in a 20-μ-thick wafer of $N_D = 2.1 \times 10^{19}$ donors/cm^3 Si:P. These preliminary single-crystal results were consistent with the anisotropies inferred from our powder sample work.

Thus aside from demonstrating the existence of anisotropic effects we have presented evidence linking the experimental linewidth and the g shift in a manner consistent with the Elliot impurity-scattering theory. The problem remains, however, of quantitatively explaining the increasingly negative g shift observed when the donor concentration is allowed to rise through the "metallic" sample range. The most reasonable starting point for such an explanation, within the framework of our "rigid-band" model, would be the work of Liu[43,44] who utilized an orthogonalized-plane-wave (OPW) calculation of spin-orbit splittings and the expressions of Roth[45] to obtain theoretical values for the principal components of the g tensor at a Si (Δ_1) conduction-band minimum. The Roth perturbation calculation was able to express these g-value components as a sum of terms involving momentum and spin-orbit matrix elements to other bands and second-order energy denominators. These denominators were of the form $E_{0\mu} \times E_{0\nu}$, with $E_{0\mu(\nu)}$ representing the energy separation between the Δ_1 band minimum and a state of identical $\vec{k}$ in the μth (νth) band. Liu[43,44] found terms of both signs contributing significantly to the shift. Nonnegligible components of the shift arose from several bands with the dominant influence being the deep but strongly spin-orbit split $2p$ bands. The principal change produced in this situation by the introduction of donor impurities in "metallic" concentrations would be the expected shift in the $\vec{k}$ values of the resonant Fermi-level electrons. If we, as a first approximation, neglect the resultant changes in momentum and spin-orbit matrix elements, the main effect of the "rigid-band" Fermi-level concentration dependence would be felt through the corresponding changes produced in the energy denominators of the Roth expressions.[45] Inasmuch as the Fermi level can rise an appreciable distance (≈ 0.07 eV for an $N_D = 10^{20}$ donors/cm^3 sample) above the undoped-band minimum, significant g-value changes may be expected as a function of concentration. Unfortunately calculations of these shifts are complicated by the need for detailed curvature information on all relevant bands. This requirement arises since the energy denominators in the g-value expressions now correspond to "vertical" differences at positions in $\vec{k}$ space displaced from that of the Δ_1 conduction-band minimum. Obviously these energy differences and hence the corresponding contributions to the g values depend critically on the differences in the local $\vec{k}$-space curvature of the bands in question. Since little quantitative information is available on this aspect of the valence bands, detailed g-value calculations appropriate to our "metallic" samples do not now seem feasible.

V. CONCLUSIONS

This work has been concerned with the careful measurement of certain parameters associated with the ESR signals arising from "metallic" phosphorus-doped silicon samples. Measured values of the spin susceptibility for $N_D \gtrsim 4 \times 10^{19}$ donors/cm^3 samples were shown to be within experimental error of those predicted on the basis of a "rigid-band" model in which all N_D unpaired donor electrons were assumed to exist in host conduction-band states. The diamagnetic component of the static susceptibility was shown to deviate from the Landau-Peierls theory in a manner roughly consistent with the results of Kjeldaas and Kohn.[4] Through the use of g-value and linewidth data, a case was made for the Holcomb-Alexander proposal[2,32] that the Fermi level rises into the host conduction band at a concentration $N_D^b = 2 \times 10^{19}$ donors/cm^3. This interpretation received further support from our observation of anisotropic g-value effects related to the silicon conduction band as well as the good agreement achieved between our linewidth results and the prediction of Elliot's impurity-scattering theory.[40]

The deviations of the spin-susceptibility temperature dependence from that expected on the basis of the "rigid-band" Pauli model indicate the existence of a non-Pauli component of the magnetism for N_D at least as high as 4×10^{19} donors/cm^3. Any such component at higher concentrations would be hidden by the accuracy limitations of the present experiment. Until a detailed analysis of our lower-concentration "impurity-banded" results is completed we shall not quantitatively speculate on the nature of this "non-Pauli" component. A treatment of the magnetism in terms of an inhomogeneous donor distribution corresponding to intermingled regions of different "average" impurity concentration seems reasonable. However recently presented evidence[15] for the rather extreme "inhomogeneity" model of Mikoshiba[46] is very unconvincing. Mikoshiba's theory attempted to interpret the present phenomena in terms of the coexistence of Pauli electrons and "isolated" neutral donors.[47] Although experimental error estimates in this work have not been given,[15] the "scatter" of adjoining experimental susceptibility vs temperature points is comparable to or greater in size than the "plateau" structure drawn on the "experimental curves."

More precise data are required if the existence of this "plateau" predicted by Mikoshiba,[46] is to be satisfactorily demonstrated. In the absence of such evidence our present inclinations are toward a much less localized interpretation of the spins responsible for the deviations from Pauli paramagnetism.

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[17] Results obtained with this method agreed within experimental error with data obtained through comparisons of (signal height) × (peak-to-peak linewidth)^2 products. This simpler comparison technique is often used (see, for example, Ref. 14) but is inherently less accurate than integration methods because of the need for very accurate linewidth measurements, and the complications introduced by small changes in the line shape.

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