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Microwave conductivity and conduction-electron spin-resonance linewidth of heavily doped Si:P and Si:As†

J. H. Pifer
Department of Physics, Rutgers University, New Brunswick, New Jersey 08903
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Results are presented of a conduction-electron spin-resonance (CESR) study of single-crystal samples of heavily doped Si:P and Si:As. By studying the CESR line shape for samples whose thickness is comparable to the skin depth, we are able to deduce the microwave conductivity $\mathrm{Re}\sigma(\omega)$. We find in Si:P that $\mathrm{Re}\sigma(\omega)$ is less than the dc conductivity $\sigma(0)$ by a factor ≈ 3 at 4.2 K for samples just below the metal-insulator transition, while above the transition $\mathrm{Re}\sigma(\omega)=\sigma(0)$. We also compare the CESR linewidths for Si:P and Si:As and find large differences which imply, contrary to many previous studies, that Elliott-Yafet relaxation via spin-orbit coupling to the host is not involved. We propose that spin-orbit coupling to the impurities is the controlling factor.

I. INTRODUCTION

Phosphorus occurs as a substitutional donor in silicon with a weakly bound electron level 0.044 eV below the conduction band. For a donor concentration $n_d < n_c \simeq 4\times10^{18}$ cm^{-3}, the dc electrical conductivity[1] $\sigma(0)$ increases as the temperature T increases, indicating thermal activation of bound electrons. At $n_d = n_c$, a metal-insulator (MI) transition[2] occurs and $\sigma(0)$ becomes almost constant. In the region $n_c < n_d < n_{cb} \simeq 2\times10^{19}$ cm^3 the Fermi level lies below the Si conduction band in an "impurity band." The shape of this band and the nature of the impurity band states are not well known. For $n_d > n_{cb}$ the Fermi level lies in the conduction band and the heavily doped Si behaves like a low-density metal.[3]

The electron-resonance[4] properties of Si:P have been extensively studied. The free carriers for $n_d > n_c$ have a strong narrow conduction-electron resonance[5] (CESR) at $g = 1.9987$ whose width increases with increasing n_d and is independent of T below 20 K.[6] For $n_d < n_c$ the electrons, although bound to the P move rapidly from site to site due to thermal agitation and electron exchange between over-lapping sites. This motion averages the hyperfine interaction with the P nucleus and a single line is still observed at the same g value. The linewidth decreases as either T or n_d increases due to motional narrowing.

Quirt and Marko,[7] and Ue and Maekawa[8] have measured the microwave (9-GHz) susceptibility χ of these electrons by integrating the CESR signal. For $n_d \gtrsim 10^{19}$ cm^{-3}, χ is substantially T independent supporting the view that Si:P can be considered as normal metal in this range. For n_d below this value, χ has a T dependence which both pairs of authors have interpreted as evidence for the persistence above n_c of localized electrons. A more likely alternative interpretation is that the enhanced susceptibility is due to electron correlation within the narrow impurity band. Recent calculations by Chao and Berggren[9] extending Brinkman and Rice's[10] $T = 0$ calculation have shown that this model gives a good qualitative explanation of the data.

In this paper we report on a further careful study of the CESR of Si:P and to a lesser extent of Si:As using single-crystal samples. For $n_d \gtrsim 10^{19}$ cm^{-3} we find the CESR is characteristic of a normal metal except that the spin diffusion which is discernible for $n_d > n_{cb}$ is several times greater than predicted by the free-electron model. By studying the line shape for samples whose thickness is comparable to the skin depth,[11,12] we are able to deduce the microwave conductivity $\sigma(\omega)$. We find $\sigma(0) = \mathrm{Re}\sigma(\omega)$ for $n_d > n_c$, but below n_c, $\sigma(0) > \mathrm{Re}\sigma(\omega)$. We discuss the meaning of these results with respect to the MI transition. Line-shape effects which we attribute to residual strains and inhomogeneities prevent us from reliably determining $\mathrm{Im}\sigma(\omega)$.

We have also measured the linewidth as a function of T and n_d in greater detail than in previous studies. By using single-crystal samples rather than powders we have reduced the effects of strain and inhomogeneity. We find that previous explanations of the broadening involving spin-orbit coupling to the Si and local moments are incorrect. Our data and in particular our comparison of Si:P and Si:As samples indicate that the important interaction involved in the broadening is spin-orbit coupling to the donors and we propose several mechanisms to explain the spin-lattice relaxation in various T and n_d ranges. We argue that our linewidth data near n_c provide evidence that local moments do not persist above n_c at least in the sense assumed in the s-d exchange model.

II. EXPERIMENTAL DETAILS

Most of the data presented here were taken on samples cut from single-crystal boules purchased from General Diode Corp., Farmington, Mass. Sample 1.0E20 was supplied by Texas Instruments. The electron concentration n was determined by measuring the room-temperature resistivity with a four-point probe and using the graph of resistivity versus impurity concentration n_d prepared by Sze and Irvin.[13] Since the starting material for these crystals was high purity ($n_a < 10^{15}$ cm^{-3}), we assume there is no compensation and $n = n_d$. We identify our samples by the measured concentration. Thus sample 1.0E20 has $n_d = 1.0\times 10^{20}$ cm^{-3}. Samples in the shape of thin rectangular slabs were cut with a wire saw with the $\langle 111\rangle$ direction perpendicular to the broad face. Other crystal orientations were random since no angular dependence was observed. For $n_d \gtrsim 10^{19}$ cm^{-3}, a typical size was $1\times 5\times 7$ mm but for $n_d \sim n_c$ much smaller samples had to be used to maintain the Q of the cavity. The samples were lapped to the desired thickness and heavily etched to a mirror finish with CP4A.[14] Most measurements were taken with the sample held on the bottom of a 9-GHz rectangular half-wave cavity with vacuum grease. For measurements on thin samples, where it was essential to excite both faces equally, two different techniques were used. Early data were taken with the sample held by Styrofoam at the center of a full-wave cavity. But since there was question whether the sample was centered accurately, later data were taken with the sample standing on edge in a dab of vacuum grease on the bottom of the half-wave cavity with the broad faces of the sample parallel to the rf magnetic field.

The CESR spectra were taken with a conventional coherent superhetrodyne spectrometer using 200-Hz magnetic field modulation. The recorded data were the derivative of the absorption signal as the external magnetic field was swept through resonance. Signal-to-noise ratios of better than 20 to 1 were achieved at 77 K with 0.1-mW incident rf power, 0.25-G peak-to-peak modulation, and 1-sec lock-in time constant. This ratio improved by at least a factor of 10 at 4.2 K. Temperatures were regulated to 0.1 K and were measured with platinum and carbon-resistance thermometers.

The temperature dependence of the resistivity was measured by a dc four-terminal technique using stainless-steel spring contacts. The geometric factor relating resistance to resistivity was determined from the room-temperature resistivity measured by the four-point probe.

III. LINE-SHAPE THEORY

Evaluation of the CESR line shape[15] for a sample whose thickness is comparable to the skin depth is simply a boundary value problem where one must calculate the rf fields inside the sample when the spins are freely diffusing. Solution of Maxwell's equation plus a modified Bloch equation[16] to describe the time dependence of the magnetization yields two wave vectors for propagation into the sample

$$k_1^2 = 2i/\delta^2 , \tag{1}$$

$$k_2^2 = 2(1+i\alpha)/\delta_e^2 , \tag{2}$$

where $\delta = (\frac{1}{2}\mu_0\omega\sigma)^{-1/2}$, $\alpha = (H - H_0)T_2$, and $\delta_e = (2DT_2)^{1/2}$. σ is the conductivity, ω is the frequency, H is the applied field, H_0 is the resonant field, T_2 is the transverse spin-relaxation time, and D is the diffusion constant. k_1 represents the usual propagation into the skin region and δ is the classical skin depth. k_2 represents the propagation of the precessing spins and δ_e is the skin depth or the distance an average spin diffuses before relaxing. For a free electron gas $\delta_e = (\frac{2}{3}v_F^2\tau T_2)^{1/2}$, where v_F is the Fermi velocity and τ is the momentum relaxation time.

The experimentally measured quantity is the derivative with respect to field of the power absorbed by the precessing spins as the magnetic field is swept through resonance. For a sample of thickness d excited with the same rf field on both faces, the resonant power absorbed is[15,17]

$$\mathcal{P} = C\,\mathrm{Im}\{u^2 \tanh^2 u[(w^2-u^2)\,\mathrm{csch}^2 u + (2u^2/w)\coth u - (3u^2-w^2)/u \coth u]/(w^2-u^2)^2\} , \tag{3}$$

where C is a constant, $u = \frac{1}{2}k_1 d$, and $w = \frac{1}{2}k_2 d$.

In a metal such as lithium, $\delta \ll \delta_e$ so that the precessing spins diffuse far beyond the skin region. In Si, due to the much lower Fermi velocity, $\delta \gtrsim \delta_e$. For thick samples where $d/\delta \gg 1$, $d/\delta_e \gg 1$, and $\delta \gg \delta_e$ (the slow diffusion limit), Eq. (3) reduces to the simple result

$$\mathcal{P} = C\,\mathrm{Im}(u/w^2) . \tag{4}$$

If the conductivity is real,

$$u = (1+i)d/2\delta \tag{5}$$

and the line shape in Eq. (4) is the sum of equal parts of Lorentzian absorption and dispersion signals rather than the pure absorption signal obtained in thin or powdered samples. Asymmetric CESR signals are customarily characterized by the

ratio A/B of the low-field peak signal to the high-field peak [see Fig. 4(A)]. Numerical evaluation of Eq. (4) gives $A/B=2.55$. If the condition $\delta_e \ll \delta$ breaks down, the signal becomes non-Lorentzian and A/B increases. Thus $A/B=2.55$ is the lower limit predicted by this theory for thick samples.

We shall see that some of our thick samples have A/B less than 2.55. This can occur if the wave vector of propagation into the skin region is not given by Eq. (5), which would happen if the conductivity were complex, or equivalently if the dielectric constant were extremely large. Interpretations that previous workers have given to their data lead us to expect a complex conductivity. To handle this possibility we set

$$u=(1+i\Gamma)d/2\delta\ , \tag{6}$$

where $\Gamma-1$ represents the degree to which the classical skin effect fails to describe the penetration of the rf fields into the sample. The thick sample CESR line shape, Eq. (4), is still Lorentzian, that is, still an admixture of Lorentzian absorption and dispersion signals, but the relative admixture is changed. Numerical calculation, Fig. 1, shows that for $\Gamma<1$ or $\mathrm{Im}(\sigma)<0$, $A/B<2.55$. Figure 1 also shows the increase in A/B that results with $\delta/\delta_e \lesssim 1$.

The observation of $A/B<2.55$ for thick samples does not unambiguously show that σ is complex since one can easily think of other mechanisms to reduce A/B. For example, inhomogeneities in the sample comparable in size to δ could alter Eq. (5) and would be indistinguishable from a complex σ. An alternative larger scale inhomogeneity that we will not consider due to the small size of our samples is a distribution of T_2 values arising from a nonuniform impurity distribution. The most likely source of altered line shapes in our samples are residual strains. Wilson and Feher[18] have shown that uniaxial stress produces a g anisotropy in Si. To evaluate the effect of strains we have calculated the line shape for a Gaussian distribution of resonant fields of width ΔH_0 which would occur for random strains in the crystal. We find that A/B is reduced from 2.55 and the line shape is only moderately non-Lorentzian for $\Delta H_0 \lesssim 0.5/\gamma T_2$. Thus unless strains are large it is not possible to distinguish their effects from a complex σ.

So far, we have been discussing samples thick compared to δ. In Fig. 2 we compare the thickness dependence of A/B for thinner samples for the various cases we have considered. Spin diffusion increases A/B for all values of d, while a complex conductivity [$\mathrm{Im}(\sigma)<0$ or $\Gamma<1$] or a distribution of g values reduces it. It is important to note that A/B is uniquely determined by d/δ for $d/\delta \lesssim 1$. By examining the CESR of a sample with $d \lesssim \delta$, one

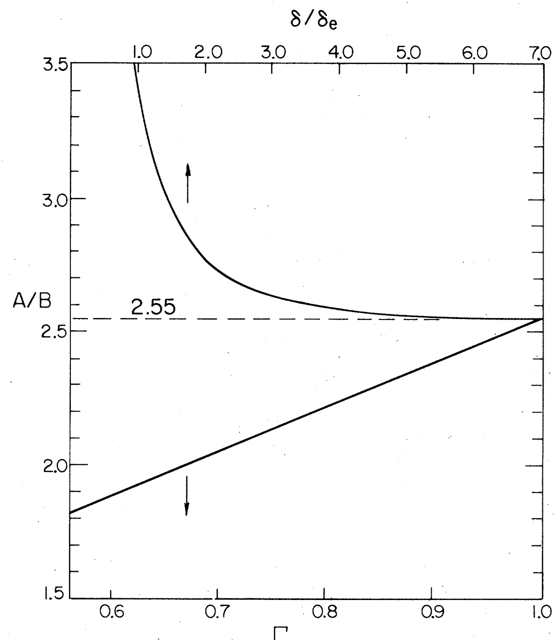

FIG. 1. Dependence of the asymmetry of the CESR line shape upon spin diffusion for thick samples and upon Γ the relative admixture of dispersion and absorption signals.

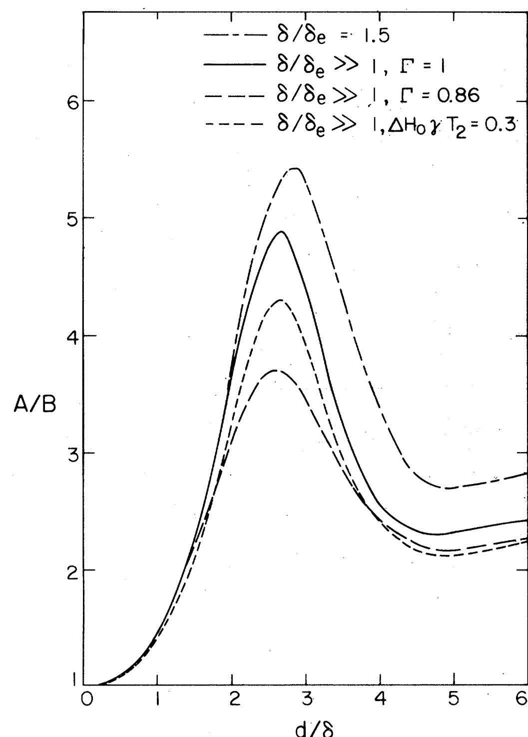

FIG. 2. Sample thickness dependence of the asymmetry of the CESR line shape.

can determine δ and thus $\mathrm{Re}(\sigma)$ even if the conductivity is complex or the sample is moderately strained. In principle one can determine $\mathrm{Im}(\sigma)$ by examining A/B for thick samples but the sensitivity to other effects shown in Fig. 2 introduces large uncertainties.

IV. DATA AND ANALYSIS

A. Line shape—$n_d \geq 10^{19}$ cm^{-3}

Microwave susceptibility measurements have shown that for $n_d \gtrsim 10^{19}$ cm^{-3}, $\chi(\omega)$ is Pauli-like as one would expect for a metal. We first discuss the CESR for samples in this concentration range. Figure 3 gives the T dependence of A/B for five typical thick ($d/\delta \gtrsim 8$) samples with $n_d > n_c$. We see $A/B > 2.55$ for $n_d > n_{cb}$. Assuming that this increase in A/B above 2.55 is due to spin diffusion, measurement of A/B uniquely determines δ/δ_e, Fig. 1. On the other hand, measurement of the linewidth and resistivity permits one to predict δ/δ_e assuming a free electron model. In Table I we compare experimental values of δ/δ_e with values deduced from

$$\delta_e = (\tfrac{8}{3}\pi)^{1/3}(m^* e^2 \gamma \Delta H \rho/\hbar^2)^{-1/2} n^{-1/6}, \quad (7)$$

which is derived assuming $\Delta H = 1/\gamma T_2$, $v_F = (3\pi^2 n)^{1/3} \times \hbar/m^*$, and $\rho = m^*/ne^2\tau$, where $m^* = 1.08 m_e$ for Si. ρ is taken from the measurements by Yamamouchi, Mizuguchi, and Sasaki,[1] where we have ignored their quoted values for n and instead used the value deduced from the room-temperature resistivity.[7,13] We see in Table I that in contrast to the experimental results, the free-electron model predicts that spin diffusion should have a negligible effect for all values of n. The disagreement is greatest for the most heavily doped samples where one would most expect the free electron model to hold and is probably the result of approximating the anisotropic conduction band with a single effective mass.

Line-shape fitting is not a conclusive test for spin diffusion since the line shape is nearly Lorentzian for the relatively slow diffusion indicated by the A/B values. Figure 4(A) compares the experimental line shape for samples 2.2E19 with the prediction of Eq. (3) when δ/δ_e is chosen to fit A/B and with a Lorentzian line shape in which the relative dispersion admixture was chosen to fit A/B. The differences are not conclusive.

For samples with 10^{19} cm$^{-3} \leq n_d < n_{cb}$, where $A/B \simeq 2.55$, the line shapes in most samples were very well fit at all temperatures by Eq. (4). A few samples had wings that were noticeably narrower than a Lorentzian. We attribute this to residual strains or inhomogeneities as will be discussed in Sec. IV B.

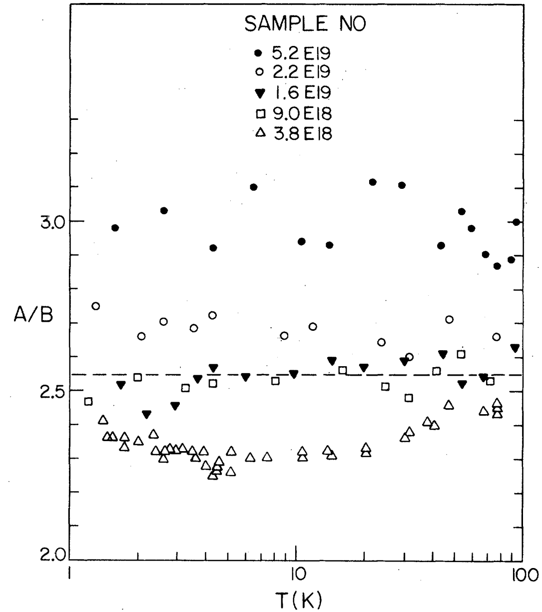

FIG. 3. Temperature dependence of the asymmetry of the CESR line shape in Si:P for various P concentrations.

B. Line shape—$n_d < 10^{19}$ cm^{-3}

Samples with $n_d \sim n_c$ can be thinned to a thickness comparable to the skin depth. We saw in Fig. 2 that for $d/\delta \lesssim 1$, A/B is determined *solely* by d/δ provided inhomogeneities, such as a distribution of g values, are small. Thus, by measuring A/B as function of T, we can obtain the T dependence of δ and hence of the microwave resistivity $\rho(\omega)$. This method has the distinct advantage that no calibration is required. Figure 5 gives A/B vs T and the derived values for $\rho(\omega)$ for three samples thinned to have $A/B \approx 1.2$ at 4.2 K. The error bars on $\rho(\omega)$ include an estimate of the variation of the thickness of the sample due to the thinning process as well as the error in measuring A/B. Since A/B becomes large at high T in sample 3.5E18, it was thinned further and A/B remeasured. The resulting values of $\rho(\omega)$ for $T > 15$ K are shown in Fig. 5 and agree well with those for the thicker sample. Also shown in Fig. 5 are the dc resistivities measured on the same samples at 4.2 and 77 K. Sample 4.5E18 is just above n_c since $\rho(0)$ slightly decreases as T decreases. We see that $\rho(0) \simeq \rho(\omega)$ within the error. The remaining two samples are below n_c since $\rho(0)$ increases as T decreases. $\rho(\omega)$ exceeds $\rho(0)$ in both samples by a factor of ≈ 2.0 at 77 K and ≈ 2.8 at 4.2 K. If we compare the T dependence of $\rho(0)$ that Yamanouchi, Mizuguchi, and Sasaki[1] obtained for very similar samples, we see that the qualitative difference in the T de-

TABLE I. Comparison of the theoretical ratio of the skin depth to the spin depth calculated using the free-electron model with the experimental ratio derived from the asymmetry of the CESR line for various donor concentrations.

				Free-electron theory				Experiment	
n_d (cm^{-3})	T (K)	ρ (10^{-3} Ω cm)	ΔH (G)	δ (μm)	δ_e (μm)	δ/δ_e	A/B	δ/δ_e	A/B
5.2E19	77	0.72	5.0	14	3.6	3.9	2.59	1.4±0.2	3.0 ±0.1
	4.2	0.65	3.8	14	4.3	3.3	2.61	1.4±0.2	3.0 ±0.1
2.2E19	77	1.2	3.0	18	4.3	4.2	2.58	3.0±0.6	2.65±0.05
	4.2	1.1	2.1	18	5.2	3.3	2.61	2.4±0.3	2.70±0.05
9.0E18	77	4.0	1.7	34	3.5	9.7	2.55	≥3.6	2.55±0.05
	4.2	2.5	1.0	27	5.7	4.7	2.57	≥3.6	2.55±0.05
4.0E18	77	9.5	1.4	56	2.6	13	2.55		
	4.2	7.4	0.3	50	6.4	22	2.55		

pendence of $\rho(\omega)$ between samples 3.8E18 and 3.5E18 is duplicated in $\rho(0)$.

The line shapes of the samples with $n_d < 10^{19}$ cm^{-3} were anomalous in two aspects. First they were frequently narrower in the wings than for a Lorentzian line. This discrepancy was generally quite small except for samples which had not been adequately etched after the surfaces were damaged by lapping. Second, in thick samples A/B was generally less than 2.55 even when the line was fairly closely Lorentzian. We can attribute some of the non-Lorentzian character to a distribution of g values arising from surface strains since heavily etching a sample generally made its CESR more Lorentzian. But this is not adequate to explain the entire effect. The A/B data for sample 3.8E18 in Fig. 3 came from three separate runs where the sample was successively thinned from 0.195 to 0.098 cm by lapping followed by a heavy etch. The excellent agreement in A/B for the different thicknesses indicates that macroscopic sample inhomogeneity, strained or damaged surfaces, or experi-

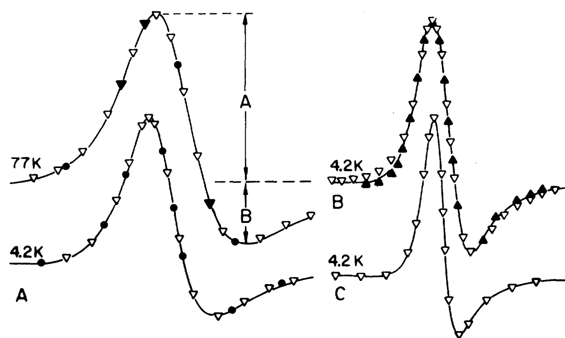

FIG. 4. Comparison of the experimental CESR line shape in Si:P with theory. Solid, experiment; ▽, Lorentzian line shape with relative admixture of absorption and dispersion (Γ) adjusted to fit measured value of A/B; ●, theory with spin diffusion; ▲, theory with a distribution of g values of width $\Delta H = 0.58/\gamma T_2$. (A) sample 2.2E18, (B) sample 4.5E18 as grown, (C) sample 4.5E18 annealed 2d at 500 °C.

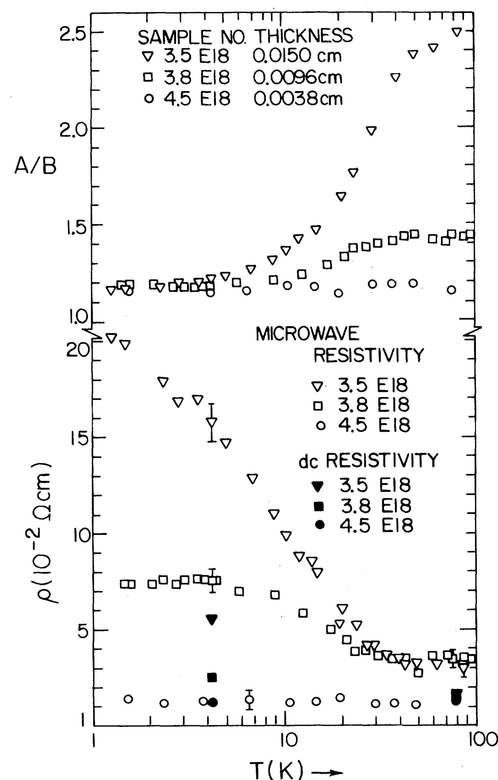

FIG. 5. (Upper) Temperature dependence of the asymmetry of the CESR line shape for thin Si:P samples near the metal-insulator transition. (Lower) Temperature dependence of the microwave resistivity derived from the A/B data and of the dc resistivity measured on the same samples.

mental effects such as the placement in the cavity or phase adjustment are not involved in the A/B anomaly in this sample. Sample 4.5E18 provides further evidence that the anomalous A/B values are not entirely due to strains in the sample. This sample as grown had an unusually low A/B—2.18 at 4.2 K—and was considerably narrower in the wings than a Lorentzian, Fig. 4(B). After being annealed for two days at 500 °C and heavily etched, the line narrowed by 10% and became perfectly Lorentzian, Fig. 4(C), with $A/B=2.57$. If we try to fit the line in Fig. 4(B) with a Gaussian distribution of g values, we need $\Delta H_0=0.58/\gamma T_2$ to fit A/B but the theoretical line is then somewhat narrower than experiment. Further, upon annealing the line should have narrowed by 50%. Thus it appears that the line shape is affected by some type of inhomogeneity that is not adequately described as a distribution of g values but which is reduced upon annealing. The most likely cause of this effect is oxygen or similar impurities. Annealing has been shown[19] to effectively remove oxygen, probably through the formation of SiO_2 clusters. This explanation is bolstered by our observation[20] that the addition of very small amounts of Fe also affects the line shape. Since the distance a spin travels before relaxing is small and the alloy is dilute, fluctuations in the number of magnetic impurities encountered by an impurity before relaxing are significant. The line-shape change due to oxygen or any magnetic impurity is then due to a distribution of g shifts and linewidths, arising from interaction with different numbers of impurities. There is no clearcut evidence that σ is complex.

C. Linewidth

The CESR linewidth ΔH that we record is the full width at half-signal of the low-field peak. The transverse spin relaxation rate $\delta_2=1/\gamma T_2$ is related to ΔH by $\Delta H=\alpha\delta_2$, where α is a constant depending upon the line shape. We have numerically calculated α for a given A/B by assuming that the line shape is Lorentzian. Most of the data we present are for thick samples with $A/B\simeq 2.55$ and $\alpha=1.03$. But for $n_d\sim n_c$, A/B varies rapidly with T and α rises to 1.23 for $A/B=1.0$.

For $n_d>n_c$ the linewidth approaches a constant value $\delta_2(0)$ at low T which is concentration dependent. If we fit $\delta_2(0)$ with a power law we find $\delta_2(0) \propto n_d^{0.6^{+0.2}_{-0.1}}$ throughout the range $7\times10^{18}\ \mathrm{cm}^{-3}\leq n_d \leq 5\times10^{19}\ \mathrm{cm}^{-3}$ with $\delta_2(0)$ falling below this value for $n_d<7\times10^{18}\ \mathrm{cm}^{-3}$. On the other hand, if we describe the concentration dependence of $\delta_2(0)$ as $\exp(-R_0/a)$ where $\frac{4}{3}\pi R_0^3=n_d^{-1}$, as originally suggested by Maekawa and Kinoshita,[6,21] we find a good fit for all $n_c<n_c<10^{20}\ \mathrm{cm}^{-3}$ with $a=10.6\pm0.8$ Å. In making these fits data for several samples supplied by General Diode and a majority of the samples made by other manufacturers were discarded because they fell considerably above the rest of the data. These samples were presumably contaminated with some impurity in addition to P.

Figure 6 compares the T dependence of δ_2 for various concentration samples. Since the low-T broadening is presumably due to a different scattering mechanism than the T-dependent broadening, $\delta_2(0)$ has been subtracted from each sample. The upper curves in Fig. 6 represent heavily doped samples with $n_d\geq1.6\times10^{19}\ \mathrm{cm}^{-3}$. We note that for high temperatures, $\delta_2(T)$ is approximately linear with T with a slope that increases with n_d. Data would have to be taken on more samples and at higher T to determine the n_d dependence. Sample 1.0E20 is anomalous in that $\delta_2(0)$ is several gauss greater than would be predicted from the trend of the other samples. If this excess broadening is due to nonelectrically active impurities and is thus independent of T, subtracting $\delta_2(0)$ makes $\delta_2(T)$ comparable with other samples.[22]

The lower part of Fig. 6 compares $\delta_2(T)$ for samples with $n_d\leq1.6\times10^{19}\ \mathrm{cm}^{-3}$. The data for sample 1.6E19 are repeated for comparison. This sample appears to represent a boundary between two types of T-dependent broadening mechanisms since δ_2 is constant up to 35 K and samples both above and

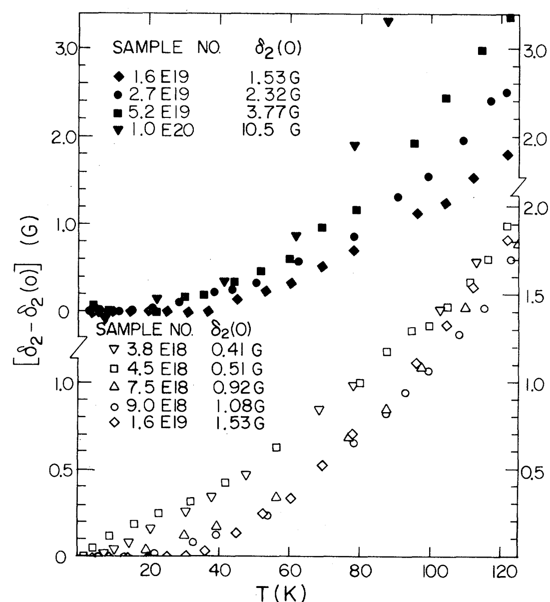

FIG. 6. Temperature dependence of the transverse spin-lattice relaxation rate in Si:P for various P concentrations. The temperature-independent relaxation rate $\delta_2(0)$ has been subtracted for each sample.

below it have greater values for $\delta_2(T)$ up to about 80 K. Note in Fig. 6 that samples near n_c have an almost linear low-T broadening.

Figure 7 compares the T dependence of δ_2 for samples near n_c. The lower curves are for Si:P and include the same three samples in which we studied $\rho(\omega)$. Sample 4.5E18 is clearly above the MI transition while sample 3.8E18 is below as indicated by the T dependence of $\rho(0)$ and the inequality of $\rho(0)$ and $\rho(\omega)$. Thus the linewidth reaches its minimum value and becomes T independent prior to the MI transition.

The increase in linewidth at low T for samples well below n_c is due to decreased motional averaging of the hyperfine interaction with the donor nuclei.[6] This narrowing becomes ineffective once a linewidth of 0.30 G is reached. For comparison we give in the upper part of Fig. 7 data for several samples of Si:As with $n_d < n_c$. The MI transition occurs at a higher value of n_d due to the greater binding energy of the As. By comparison with the Si:P CESR we estimate $n_c = (7.5 \pm 0.5) \times 10^{18}$ cm^{-3} for Si:As. The broadening is observed to be much stronger and the minimum linewidth is 2.6 G. The linewidth at 77 K for the three Si:As samples is $\delta_2 = 10.5$ G which compares with $\delta_2 = 1.36$ G at 77 K for the three lowest doped Si:P samples. We attempted to observe the CESR in several samples of Si:Sb near n_c but could find no resonance, indicating $\delta_2 > 100$ G.

The orientation dependence of the linewidth at 4.2 and 77 K was examined for several samples of Si:P near n_c and n_{cb}. The line was isotropic within our experimental error of 5%. One would expect[18] a small anisotropy in a badly strained crystal due to the g anisotropy of a single conduction-band valley.

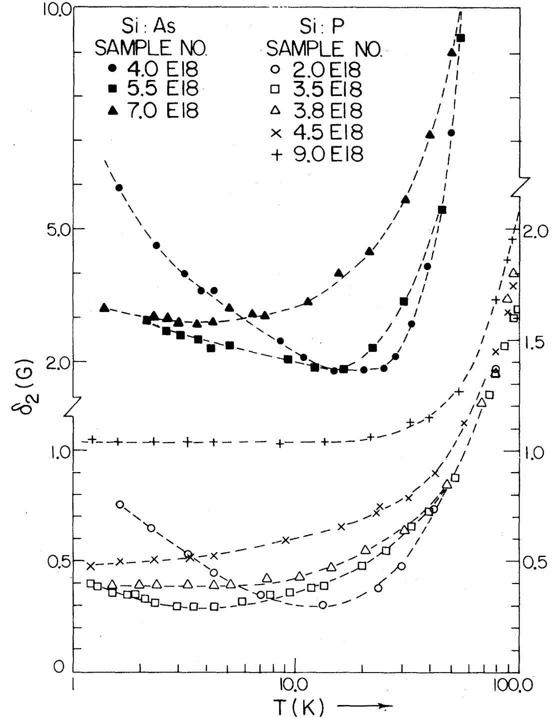

FIG. 7. Temperature dependence of the spin-lattice relaxation rate for Si:P and Si:As for samples near the metal-insulator transition.

V. DISCUSSION

A. Linewidth for $n_d > n_c$

Elliott[23] and Yafet[24] (EY) have studied spin-lattice relaxation of conduction electrons in semiconductors. They assumed that *spin-orbit coupling to the host* admixes a small amount of spin of the opposite orientation into the conduction band Bloch states. Scattering of a conduction electron into another Bloch state by either an impurity or a lattice phonon results in spin-lattice relaxation since the relative admixture of spin states is changed. Since spin-orbit coupling to the host also produces a shift Δg of the CESR g value from the *free electron value,* EY found a correlation with the spin lattice relaxation time T_1 of the form

$$1/\gamma T_1 \propto \Delta g^2/\tau , \tag{10}$$

where τ is the momentum relaxation time due to either phonon scattering, or to impurity scattering τ_i. At low T, τ_i predominates and $1/\gamma T_1$ becomes independent of T. Note that this theory predicts that the CESR broadening should be practically independent of the type of donor since scattering due to lattice phonons is totally independent of the impurity content while the scattering from ionized donors is the same for all donors of the same charge if, for example, one assumes a screened Coulomb potential. Experimentally[25] there is about 10% difference at room temperature in τ_i for Si:As and Si:P due to differences in the core states.

Asik, Ball, and Slichter[26,27] (ABS) have shown that the T-independent broadening of the lithium CESR is not due to EY relaxation but to *spin-orbit coupling to the impurity,* which admixes spin states and causes transitions between Bloch states. ABS predict that the broadening should vary as $n_d \rho(E_F)$, where $\rho(E_F)$ is the density of states at the Fermi level. In Si:P, $\rho(E_F)$ should vary as $n_d^{0.2-0.3}$ depending upon the model[28] used. Thus, the broadening should vary at least as rapidly as $n_d^{1.2}$. There is no connection between Δg and T_1 since the electrons spend most of the time away from the impurity.

There have been numerous attempts[7,8,29,30] to fit the EY theory to the CESR in Si:P assuming $T_1 = T_2$.

The consensus has been that there is qualitative agreement between theory and experiment. However, all the studies which included low-T data have postulated some additional broadening mechanism. Quirt and Marko[7] (QM) assumed a broadening in their powdered samples produced by the anisotropic g tensor associated with one conduction band valley. This can occur provided the scattering time around the Fermi surface is not extremely long, only if large strains substantially shift the valley populations.[18] However, their etching and annealing procedure should have eliminated the strains introduced in powdering. Ue and Maekawa[8] (UM) assumed the presence of localized moments and a Korringa broadening linear in T. Our data in Figs. 6 and 7 do not show a linear broadening at low T except possibly near n_c. Gershenzon, Pevin, and Fogelson[30] suggested an additional T-independent broadening due perhaps to an inhomogenous impurity distribution. In contrast to these studies our data do not even qualitatively agree with the EY theory since the broadening depends strongly upon the type of impurity. The much greater broadening at both low and high T in Si:As compared to Si:P and our failure to see a CESR in Si:Sb strongly suggest that the relaxation involves spin-orbit coupling to the impurity.

It is clear from our data that several relaxation mechanisms are involved with different T and n_d dependences. We propose that our data can be explained, at least qualitatively, by a combination of the EY and ABS models plus a new relaxation mechanism. We first consider the T-independent linewidth. In the ABS model the electron only rarely encounters an impurity. The spin-lattice relaxation rate is then given by the probability of spin flip per collision, which is independent of n_d, times the number of collisions with an impurity per second. Since the electron moves through the lattice at a constant velocity, the number of collisions per second is just proportional to the concentration of impurities. In metallic Si an electron is always "near" a donor in order to provide screening. It would seem that correlations in the electron scattering should be considered. We can, however, obtain a n_d dependence close to the experimental result by neglecting interatomic correlations in the spirit of the Hubbard model and assuming that the probability of spin flip per collision with an impurity is independent of n_d. The time between collisions is simply the time for an electron moving at the Fermi velocity to travel the distance between impurities. Then we expect $1/T_1 \propto v_F/2R_0$. Assuming free electrons, $v_F \propto n_d^{1/3}$ thus $1/T_1 \propto n_d^{2/3}$. Note that with such a short collision time, $\approx 2\times10^{-11}$ sec, a spin-flip probability of only $\approx 10^{-4}$ per collision is needed. It remains for detailed calculations to verify that the spin flip probability does not depend on n_d. It should be noted that the Born approximation is not adequate since the screening length $a_s < 1/k_F$, where k_F is the Fermi wave number.[31,27] Since the linewidth data is fit over a wider range with $\exp(-R_0/a)$ than with a power law, it may be that the concentration dependence simply arises from overlap of tight-binding wave functions.

We next consider the T-dependent broadening. For samples with $n_d \leq 8\times10^{18}$ cm^{-3} the linewidth is independent of n_d at high T but does depend upon the type of impurity. (To be absolutely sure of this asymptotic behavior, data should be taken to a much higher T.) A straightforward explanation of this data is modulation of the spin-orbit coupling to the impurity by thermal vibration of the impurity—that is by the EY mechanism with the impurity spin-orbit coupling substituted for the host spin-orbit coupling.

For samples with $n_d > 8\times10^{18}$ cm^{-3}, Fig. 6, the T-dependent broadening depends upon n_d. We suggest that this is due to spin-orbit coupling to neighboring impurities. This coupling is not necessarily smaller than to the central impurity since only non-s-like components of the wave function couple to the central core, while all components can couple to neighboring cores. This contribution should increase as R_0 decreases due to greater overlap. Thermal vibration of the impurities modulates the coupling and produces the T-dependent broadening.

This spin-orbit coupling to neighboring impurities might also explain the concentration-dependent g shift observed[29,7] in Si:P for $n_d \gtrsim 10^{19}$ cm^{-3}. In which case, there should be a correlation between the linewidth and the g shift from the g value for $n_d < 10^{19}$ cm^{-3}. EY predicted a correlation with the g shift from the free-electron value. Unlike EY this mechanism predicts a much stronger n_d dependence in Si:As than in Si:P since the broadening is stronger. However, this broadening will make it hard to measure the g shift accurately.

Consideration of g shifts points up a serious problem with models involving spin orbit coupling to the central impurity. In insulating silicon, P, As, and Sb all have a g shift of about -35×10^{-4} from the free-electron value due to spin-orbit coupling to the host. There is an additional g shift of about 2×10^{-4} that depends upon the type of impurity[5] and is due to spin-orbit coupling to the impurity core. Then if the central impurity coupling is so small relative to the host coupling, why does the EY relaxation not predominate? It may be that formation of the impurity band with a strong p-like component greatly increases the spin-orbit coupling to the donor and that the random distribution of impurities prevents there from being a corres-

pondingly large g shift of the CESR. On the other hand, it is possible that a different model involving the impurity in some other manner is required. Another open question is whether the proposed model can explain the rather strong magnetic field dependence of ΔH reported by UM and QM for heavily doped samples. At this point detailed calculations are necessary. *(See note added in proof.)*

We turn to the question of the persistence of localized moments in Si above n_c which came initially from magnetoresistance data.[3,32] UM and QM have interpreted their microwave susceptibility data in terms of a two component model involving localized moments.[33] We will first consider whether our linewidth data provide any evidence for local moments. Following UM we assume Hasegawa's model[34] of separate d and s systems strongly interacting (bottlenecked), then the linewidth[35,17] should be

$$1/T_{1\,\mathrm{eff}} = (1/T_{sl} + \chi_r/T_{dl})/(\chi_r + 1)\,, \tag{11}$$

where T_{sl} and T_{dl} are the spin-lattice relaxation times of the conduction electrons and localized electrons. χ_r is the ratio of the susceptibility χ_d of the localized electrons to the susceptibility χ_s of the conduction electrons. UM attempted to fit their linewidth data to $T_{1\,\mathrm{eff}} = T_{sl}/\chi_r$, which is linear in T if the Curie-Weiss temperature is small. This equation is obtained from Eq. (11) by assuming $T_{dl}^{-1} = 0$, which does not appear to be generally true, and $\chi_r \gg 1$. From their data one can see that this latter assumption is true at best only up to 10–20 K. Above 20 K, χ_r becomes small and Eq. (11) predicts $T_{1\,\mathrm{eff}} = T_{sl}$. Thus the UM interpretation of the approximately linear increase in linewidth up to 80 K is incorrect. If we are to see an effect on the linewidth by the local moments, it must show up chiefly below 20 K where χ_r is large. Yet for most of our samples ΔH is constant below 20 K. From Eq. (11) this can occur only for $T_{dl} = T_{sl}$. The other alternative, $T_{dl} \ll T_{sl}$, is ruled out since it would predict a decrease in ΔH above 20 K. The g value is also independent of T in the low-T range. Since g is given by an equation analogous to Eq. (11), this implies that the conduction electrons and the localized electrons have the same g value. Thus there seems to be no justification for assuming separate localized electrons since the g value and relaxation rate are identical to those of the conduction electrons. Our samples near n_c do show a small T-dependent broadening below 20 K, Fig. 6. However, the excess broadening compared to more heavily doped samples persists to a temperature well above the region where χ_r is large. Further as n_d increases, the broadening first disappears at low T which is exactly opposite to the behavior predicted by Eq. (11). Our line-shape data would not be expected to show evidence for localized moments since our calculations[17] based on the s-d exchange model have shown that strong coupling to localized moments produces no change in the CESR line shape.

We thus conclude that the linewidth data provide evidence that *local moments do not persist above* n_c as a separate species in the sense of the Hasegawa model. Further, since the inhomogeneity model proposed by QM and UM seems to require a treatment something like the sd exchange model, we feel the model is inconsistent with the linewidth data.

We emphasize that our data do not provide evidence against an inhomogeneous electron distribution in the sample. In fact, nuclear resonance studies[36] of the P show a static distribution of Knight shifts, presumably due to inhomogeneity in the electron distribution. CESR is not sensitive to small scale inhomogeneity since a spin typically diffuses several μm before relaxing (see Table I). Our data merely show that it is not meaningful to regard some of the resonating electrons as a separate well defined class possessing a localized moment.

B. Model of the metal-insulator transition

The theoretical situation is still speculative and detailed calculations are only now appearing. But we will adopt the following picture[2,37] which seems to be gaining support. The most important factor determining the ground state of the P donor electrons is the intra-atomic correlation arising from the penalty in Coulomb energy that must be paid when two electrons (of opposite spin) are located on one P site. Thus the ground state for lightly doped material consists of singly occupied P sites with equal numbers of spin-up and spin-down electrons randomly distributed. As the number of impurities increases, the exchange between neighboring impurities broadens the singly and doubly occupied electron states into two Hubbard bands[38] separated by the correlation energy with the lower band fully occupied at $T = 0$. Further increase in the overlap between neighboring impurities broadens the bands until the gap disappears at the Mott critical density. The random distribution of impurities causes Anderson[39] localization at the edges of the Hubbard bands. Thus even though the bands have merged, the MI transition does not occur until the Fermi level crosses a mobility edge in the upper Hubbard band.

This description in terms of Hubbard bands (as distinct from the Hubbard Hamiltonian) is not adequate for the metallic state since it does not properly treat the Fermi surface. Starting with the Hubbard Hamiltonian, Brinkman and Rice[10] have

described the highly correlated metallic state electron gas in terms of a variational ground state in which correlation reduces the amplitude of doubly occupied states as the metallic state is approached from the metallic side. Chao and Berggren[9] have shown that this model gives a good qualitative account of the T dependence of the susceptibility. Here the non-Pauli susceptibility arises not from fluctuations in the random distribution of impurities, but from occupation of impurity sites by a single electron due to correlation.

In Secs. V C and V D we will interpret our data in the simplest way—free electrons with a scattering time τ and effective mass m^*. Then we shall see how the details of the model we have just presented enter into the interpretation.

C. Drude-Zener model of the conductivity

We observe that below n_c, $\sigma(0)/\mathrm{Re}[\sigma(\omega)]>1$, Fig. 5. D'Altroy and Fan[40] observed similar behavior in n-type Ge which they discussed in terms of the Drude-Zener model,[41] in which the electrons move with effective mass m^* and momentum relaxation time τ. If τ^{-1} is comparable to the frequency, the real part of the microwave conductivity

$$\sigma(\omega)=\sigma(0)/(1+i\omega\tau) \tag{8}$$

exceeds $\sigma(0)$. At 4.2 K, Eq. (8) yields $\tau\approx 2.5\times10^{-11}$ sec for samples 3.5E18 and 3.8E18 while $\tau<10^{-11}$ sec for sample 4.5E18. Then using $\sigma(0)=ne^2\tau/m^*$, we obtain effective masses of $140m_e$, $70m_e$, and $<20m_e$, respectively, for the three samples, where we have taken $n=n_d$ to obtain an upper limit on m^*.

Equation (8) also predicts an imaginary component of σ which should show up in the line shape of thick samples given by Eq. (4), where u is given by Eq. (6) with $\Gamma\neq1$. For sample 3.8E18 at 4.2 K, $\sigma(0)/\mathrm{Re}\sigma(\omega)=2.9$ implies that $\omega\tau=1.4$ or $\Gamma=0.33$. This should reduce A/B to 1.45. We find instead that $A/B=2.26$ which would correspond to $\Gamma=0.82$ if no strain or inhomogeneity effects are present. But as we discussed in Sec. IV B, these effects are so large we cannot be sure we are seeing any effect at all due to complex σ. Before we rule out the Drude-Zener model we must consider whether we are justified in neglecting the displacement current. If the dielectric constant ϵ is large, we must replace $\sigma(\omega)$ with an effective complex conductivity $\sigma'(\omega)=\sigma(\omega)+i\omega\epsilon$. Since $\mathrm{Im}[\sigma(\omega)]<0$, a large ϵ would reduce $\mathrm{Im}[\sigma'(\omega)]$. In Si at 9 GHz we get $\sigma(\omega)/\epsilon\omega=340$, assuming $\epsilon=11.4$. However, Bethin, Castner, and Lee[42] have noted that due to the polarization catastrophe ϵ should diverge as the metal insulator transition is approached. They have found $\epsilon\sim20$ for $n_d=2.2\times10^{18}$ cm^{-3} for Si : P. Using their derived value for the polarizability α_D in the Clausius-Mosotti relation, we would expect $\epsilon\sim29$ for $n_d=3.8\times10^{18}$ cm^{-3}. However, this approach is dubious since α_D should depend on n_d near n_c and in fact their value for α_D predicts a critical concentration of 1.1×10^{19} cm^{-3} rather than 4×10^{18} cm^{-3}. To explain our data for sample 3.8E18 we would require $\epsilon\sim3300$. This seems extreme since density fluctuations should smear out any divergence at n_c. Also samples with smaller n_d should show larger decreases in A/B since the cancellation of $\mathrm{Im}[\sigma]$ by the displacement current should be much less complete. For sample 3.5E18 we were not able to examine a thick sample since δ becomes very large at low T due to the freezing of carriers. However, for thinner samples we did find $A/B\gtrsim2.0$ indicating that we are not seeing the effect of $\mathrm{Im}(\sigma)$. Thus it is unlikely that the Drude-Zener model gives a correct explanation of the reduced microwave conductivity.

There are several complications which cloud the interpretation of our $\rho(\omega)$ data in terms of the correlation model. First a magnetic field of about 3000 G is applied during the measurement since we are using the CESR as a probe of the skin depth. The dc magnetoresistance is at most a 1% effect[3] and lacking contrary evidence we assume this is true at 9 GHz. Second dc resistance changes have been observed[43] in Si : P upon application of resonant microwave power, presumably due to the excitation of carriers. Since we do not see any change in our CESR signal with microwave power ($\lesssim0.1mw$), we feel this effect makes a negligible contribution. Thus it seems that the explanation of $\rho(\omega)$ is a clearcut test of the model. Since $\rho(0)=\rho(\omega)$ for sample 4.5E18, which is clearly just above n_c, it seems that the anomalous values for $\rho(\omega)$ cannot be produced by correlation effects or exchange scattering[44,45] with singly occupied impurities. Experimentally, it is important to determine the frequency dependence of $\rho(\omega)$ to help clarify the mechanism involved.

D. Linewidth near n_c

Well below n_c the CESR linewidth increases at low T (see samples 2.0E18 and 3.5E18 in Fig. 7). If this broadening is due to reduced motional narrowing as the thermal activation of the carriers decreases, we can estimate δ_2 from[46]

$$\delta_2=H_z^2\gamma\tau_c\,, \tag{9}$$

where we assume that as the electron moves from site to site with correlation time τ_c it experiences a field that varies randomly between the values $\pm H_z$. We assume H_z is due to hyperfine interaction with the donor nucleus. For P with $I=\frac{1}{2}$, $H_z=\frac{1}{2}A=21$ G.[5] We estimate $\tau_c=2R_0/v_F$, where $\frac{4}{3}\pi R_0^3=n_d^{-1}$ and v_F is the Fermi velocity for a free-electron band having n_d electrons with the effective mass m^* we

derived using Eq. (8). At 4.2 K this procedure gives $\delta_2 = 0.15$, 0.07, and 0.007 G for samples 3.5E18, 3.8E18, and 4.5E18. We actually expect the narrowing to be even stronger than this since we apparently do not observe the effects of a complex σ as would be implied by such large effective masses. Thus it is clear then that incomplete narrowing of the hyperfine lines can explain the low-T-broadening, but that the narrowing is stopped near n_c by a T-independent broadening mechanism such as discussed in Sec. V A. In Si:As, $A = 71$ G and $I = \frac{3}{2}$ so that the average H_z is 71 G and Eq. (9) predicts that for a given value of τ_c, δ_2 should be ≈ 10 times larger in Si:As than Si:P. We see in Fig. 7 that this is indeed the case provided samples 2.9E18 and 4.0E18 have τ_c comparable to the values for Si:P. We note for a narrowed line the spin-lattice relaxation time T_1 exceeds T_2 as long as $\tau_c > 1/\omega_0 = 1.8 \times 10^{-11}$ sec.[24] For $\tau_c = 1/\omega_0$, Eq. (9) yields $\delta_2 = 0.14$ G for P. Thus we expect that near n_c narrowing is sufficient to make $T_1 = T_2$.

The most striking feature of our data for a given sample below n_c is the qualitative similarity of the T dependence of $\rho(0)$, $\rho(\omega)$, and δ_2 below 20 K. This is perhaps to be expected since both δ_2 and ρ are determined by motion of electrons through the sample. But it is difficult to make this connection for several reasons. First the CESR can be narrowed by exchange between filled electron states which would have no effect on the resistivity. We see evidence for exchange narrowing at low T.

Second, CESR is sensitive to all of the electrons and in particular to slowly moving electrons which would contribute little to the conductivity but would make a large contribution to the linewidth.

We believe our samples have very low compensation and the similarity of ρ and δ_2 simply arises from the need for thermal activation (with energy ϵ_2) to create empty electron states in the lower Hubbard band. Once these holes exist, there are differences in the way the motion affects δ_2 and ρ, but they do not have a strong effect on the qualitative appearance of the data. We leave a detailed comparison of the linewidth data and the resistivity to a separate paper.[47]

In sample 3.8E18, $\rho(\omega)$ and $\rho(0)$ are independent of T. Mott[2] has suggested for $\rho(0)$ that the apparent T independence is due to a transition to variable range hopping with a very slow ($\ln(\rho) \propto T^{-1/4}$)$T$ dependence. We have suggested that the T independence of δ_2 occurs because the (thermally activated) motion of an electron is sufficiently rapid that the lifetime is determined by spin flip scattering from the P impurities it encounters. Since δ_2 and $\rho(0)$ both reach T independence in the same concentration range we suggest that scattering rather than variable range hopping predominates in the resistivity.

In summary we feel that unlike $\rho(\omega)$, measurement of the CESR linewidth provides little information about the MI transition that is not obtainable from the dc resistivity.

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Note added in proof. J.-N. Chazalviel has recently theoretically considered the spin relaxation in heavily doped Ge [J. Phys. Chem. Solids 36, 387 (1975)] and InSb [Phys. Rev. B 11, 1555 (1975)]. In the case of Ge he has considered a core-potential Elliott relaxation process, where in addition to the usual screened Coulomb potential, the rapidly varying impurity core potential is taken into account. He shows that this T-dependent process is $\approx 10^2$ more effective in Ge than the usual Elliott relaxation, has a $n_d^{2/3}$ concentration dependence, and depends strongly upon the type of donor. Chazalviel suggests that this mechanism accounts for the CESR linewidth in Si. In the region where ΔH depends on T our data do not appear to have such a simple concentration dependence. However, it should be possible to extend these ideas to low temperatures to explain the T-independent linewidth which does have the $n_d^{2/3}$ concentration dependence.

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