Electron Spin Resonance in n-Type InSb†

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Experimental data on the g value of conduction electrons in InSb are presented for concentrations over the range 3.6×10^{13}/cm³ to 1.5×10^{16}/cm³ at 9 and 35 Gc/sec. Agreement with existing theory is fairly good. The experimental effective mass for the electrons at $k=0$ is $0.0136m_0$. Linewidth-versus-concentration data are included, the narrowest lines (0.3G) occurring at about 5×10^{14}/cm³. Also included are estimates placing an upper limit of 5×10^{-7} sec on the electron spin-lattice relaxation time T_{1e}.

INTRODUCTION

THE conductor-electron spin resonance of InSb was first observed by Bemski.[1] He showed that the g value decreases with increasing electron density over the range 10^{14} to 10^{15} electrons/cm³ in agreement with theory. We have improved on these measurements by using better samples over a wider range of concentrations and find minor deviations between experiment and theory at concentrations above 10^{15} electrons/cm³. The linewidth ΔH shows a pronounced narrowing in the region of 4 to 5×10^{14} electrons/cm³ and is only 0.3 G in contrast to published measurements of other authors.

Also reported here are attempts to measure the electron spin-lattice relaxation time T_{1e} by two different methods. The first is a conventional saturation method. The second is to observe the ESR amplitude near an electron injection contact at one end of a bar sample, and look for a difference in the ESR amplitude for positive and negative currents. No T_{1e} could be measured but a reasonable upper limit suggested by the experiments is less than 5×10^{-7} sec in contrast to a previously published estimate.[2]

ACCURATE g VALUES AND LINEWIDTHS

Data were taken at both 9 and 35 Gc/sec. Figure 1 shows the g values obtained. Most of the samples shown were produced by neutron doping (thermal neutron transmutation of In into the donor impurity Sn).[3] The samples were annealed to decrease damage caused by the neutron irradiation. At concentrations below 10^{15} electrons/cm³, p-type impurity introduction was often a problem and the annealing was done at 385°C or lower. Very homogeneous Hall bars were obtained and after accurate electron concentration measurements, small sections were removed for ESR g-value and linewidth measurements. Table I gives the g-value measurement errors.

It should be mentioned that the g value of the conduction electrons in InSb depends on the microwave power if the power is sufficient to produce hot electrons.[4,5] The values of Fig. 1, of course, were measured at low powers where the g value is independent of power.

The linewidth versus concentration is shown in Fig. 2. Annealing the samples often reduced the linewidth by a factor of 2. It is not certain that these linewidths are really the minimum obtainable, but they are selected from nearly 50 specimens from several different sources. Each of the points of Figs. 1 and 2 (except the 3.6×10^{13} sample) actually represent several samples that gave nearly the same g values and linewidths. The most important factor for a narrow line seems to be proper annealing of the cut specimen. A second important factor, especially at high concentrations, is etching the sample surface. CP4A is used and usually followed by an alkaline etch H-100.[6]

Because of the increasing nonparabolicity of the conduction band at concentrations of 10^{16}/cm³ and higher, a more generalized form of the Roth formula[7] than that used by Bemski is necessary to calculate the g value

$$g=2\left[1-\left(\frac{m_0}{m^*(k)}-1\right)\frac{\Delta}{3(E_g+E_f)+2\Delta}\right], \quad (1)$$

where E_g is the energy gap (0.235 eV), Δ is the spin-orbit splitting, m_0 the free-electron mass, and $m^*(k)$ the electron effective mass at the Fermi level E_f. This is the momentum effective mass as defined by

$$1/m^*(k)=(1/\hbar^2k)(\partial E/\partial k), \quad (2)$$

where $m^*(k)$ is related to the electron concentration by the relation[8]

$$m^*(k)=m^*(0)[1+2\hbar^2k^2/E_gm^*(0)]^{1/2}. \quad (3)$$

Using Eq. (3) along with the equation for E_f versus k

$$k=\{[2m^*(0)/\hbar^2]E_f(1+E_f/E_g)\}, \quad (4)$$

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the effective mass $m^*(k)$ and Fermi energy versus concentration are calculated and the theoretical g-value curve shown in Fig. 1 is obtained. These experimental data of Fig. 1 give a g value at $k=0$ of 51.3 ± 0.1.[9] Using the values $\Delta=0.98$ eV and $E_g=0.235$ eV, the experimental effective mass at $k=0$ is 0.0136 m_0. To our knowledge Δ has not yet been measured accurately by experiment but theories give it values ranging from 0.78 to 0.98 eV.[10–12] Fortunately, as seen in Eq. (1), the dependence on Δ is weak. We find somewhat better fit between experiment and theory at higher electron concentrations if 0.98 eV is used. If the value 0.87 eV were used, the experimentally determined

TABLE I. Experimental errors for InSb g value versus concentration data.

Concentration n (cm^{-3})	g value	Linewidth (G)	Freq. (Gc/sec)
$3.6\pm0.3\times10^{13}$	-51.31 ± 0.1	4.0	9
$6.4\pm0.1\times10^{13}$	-51.25 ± 0.05	1.7	9
$4.9\pm0.1\times10^{14}$	-50.59 ± 0.02	0.40	9
	-50.61 ± 0.03	0.52	35
$5.0\pm0.1\times10^{14}$	-50.57 ± 0.02	0.33	9
$1.8\pm0.05\times10^{15}$	-49.48 ± 0.1	2.0	35
$1.2\pm0.1\times10^{16}$	-44.75 ± 0.3	10.8	35
$1.5\pm0.1\times10^{16}$	-43.4 ± 0.4	15	35

effective mass would be 0.0132 m_0. Also, a larger value of $m^*(0)$ gives better agreement with other types of experiments such as Faraday rotation[13] and magneto-absorption.[14] However, in most of these experiments it is necessary to extrapolate to zero magnetic field. In ESR experiments the field is very low: 500 G at 35 Gc/sec and 125 G at 9 Gc/sec. As shown in Table I the g value of one sample (4.9×10^{14} electrons/cm^3) was measured at both 9 and 35 Gc/sec with no significant difference. The extrapolation to zero field here should be reliable. Measurements of the effective-mass shift with high magnetic fields[15] suggest a roughly linear

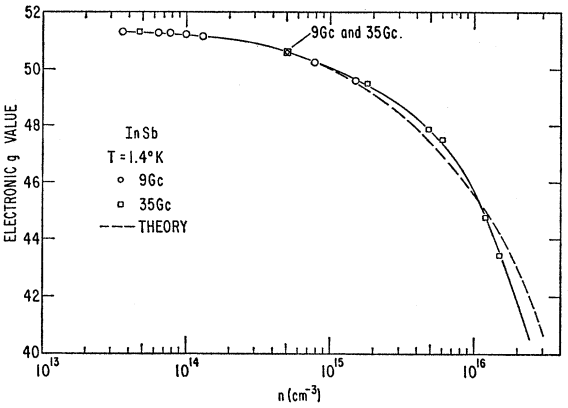

FIG. 1. Comparison of experimental g values for conduction electrons in InSb with theory. The electron concentrations were measured at 77°K. The small deviation between the two at high concentrations is unexplained.

g shift with magnetic field of 0.2 per kG for fields above 10 kG. This would require the g value (absolute value) to be about 0.08 *smaller* at 35 Gc/sec than at 9 Gc/sec. We find the 35-Gc/sec value to be 0.02 *larger*, but this is less than the experimental error of 0.03, so not very reliable. Nevertheless, the dependence of the g value [or $m^*(k)$] on magnetic field seems to be weaker at fields below 1 kG than at higher fields.

At concentrations below 4×10^{14} cm^{-3} the InSb resonance line becomes increasingly broad. This could be a case similar to phosphorus-doped silicon.[16] In the case of Si, as the donor concentration is lowered the conduction electrons begin to localize around impurity centers and hyperfine broadening occurs. Such inhomogeneous broadening produces a Gaussian line shape.

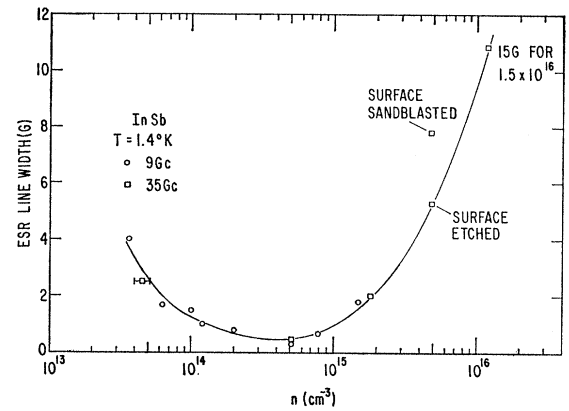

FIG. 2. Conduction-electron spin resonance linewidth of InSb versus electron concentration for carefully prepared samples. At low concentrations the line is broadened presumably due to localization of some of the conduction electrons around the donor sites.

[9] This agrees very well with M. Gueron (Ref. 5, p. 443), who obtained 51.4 at $T=0$ by extrapolation of ESR g values versus temperature for a sample with $n=2\times10^{14}$/cm^3 and frequency of 35 Gc/sec.

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We have not found any pure Gaussian line shapes in the purer InSb but there could still be some hyperfine broadening occurring. Another similar broadening mechanism could be due to an effect of localized spins in InSb at low electron concentrations.[17] These quasi-localized spins are effective in scattering both conduction electrons and phonons and produce negative magnetoresistance and thermoelectric power anomalies. Khosla and Sladek have deduced that for an electron concentration of 4×10^{14} cm^{-3} about 5% of the electrons have become localized at 1.3°K. Purer samples should have even more localized electrons. The negative component of magnetoresistance is found to decrease on raising the lattice temperature from 1.4 to 4°K because some localized electrons are ionized by the thermal energy. The ESR data are consistent with this picture. Samples with about 6×10^{13} electrons/cm^3 show a slight narrowing of the resonance (about 10–20%) when either the temperature or microwave power is increased. Unfortunately the effect is small and the ESR signal-to-noise ratio for these pure samples is too poor to do really quantitative experiments. Also, the narrowing is accompanied by the usual g shift, and as the power is increased still further, the line broadens and disappears.

ATTEMPTS TO MEASURE T_{1e}

It would be desirable to measure the conduction-electron spin-lattice relaxation time T_{1e}. Nuclear polarization experiments done in this laboratory[18] require an estimate of T_{1e} to understand the various mechanisms of polarization. Some estimates have indicated that T_{1e} might be as long as 10^{-4} sec.[2] Our ESR experiments place an upper limit on T_{1e} of 5×10^{-7} sec and possibly an order of magnitude shorter than this.

The first method used to measure T_{1e} was the conventional saturation method. This method, however, can only give an upper limit for T_{1e} because of the hot-electron effects mentioned earlier. At high powers the g value decreases, the line broadens, and the amplitude decreases. These hot-electron effects occur before any true saturation can be observed. Taking for the minimum power at which saturation could occur that at which hot-electron effects start, an upper limit for T_{1e} of 5×10^{-7} sec obtained for a sample with $n=5\times10^{14}$/cm^3. This assumes the validity of the well-known saturation parameter of magnetic resonance.

The second method used to try to measure T_{1e} made use of a microwave "window" inside a 35-Gc/sec cylindrical cavity. The sample was a thin bar with current leads soldered to each end. The microwave window limited ESR sensitivity to a section of the bar about $\frac{1}{2}$ mm long. The sample could be moved so the ESR signal at any $\frac{1}{2}$-mm section along the bar could be observed. The ESR line was usually observed with the window near one of the current contacts and the traces for positive and negative currents compared. If electrons were being injected one would expect a smaller signal, since it should take a finite time ($\sim T_{1e}$) for the injected metallic electrons (with $g=2$) to assume the spin equilibrium of the new environment of the InSb crystal ($g\simeq-50$). Reversing the current should give a larger signal since the electrons would be traveling a greater distance before taking part in the ESR at the opposite end of the sample at the location of the microwave window. Observation of this effect was attempted on three samples of concentrations ranging from 5×10^{13} to 3×10^{15}/cm^3. No difference in the ESR signal was ever observed for positive and negative currents. Simple calculations—involving carrier drift velocity, the relevant dimensions such as window size and position, and the signal-to-noise ratio—give a minimum detectable T_{1e} of from 1 to 3×10^{-7} sec depending on the concentration. There is no certainty that this is a valid method to measure T_{1e} since the conditions at the contact might be such as to preclude the observation of such an injection effect. The injected metallic electrons might be almost immediately equilibrated to the new g value of -50 because of complicated conditions associated with the contact region, in which case a long T_{1e} would not be observable by this method. Several types of contacts were tried in the experiments. One reasonable method used cleanly cleaved contact surfaces with evaporated In for a large-area (1-mm^2) contact. Another method used Te-doped In solder.

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