# Measurement of Conduction-Electron-Spin Relaxation in Sodium, 14–20 K[*]

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Conduction-electron-spin relaxation in sodium has been measured in the liquid-hydrogen-temperature range 14–20 K. We believe we have successfully separated the contributions to the measured relaxation rate from the impurity, surface, and electron-phonon (intrinsic) mechanisms by working with samples of controlled geometry at low rf frequency (10 MHz). The temperature dependence of the intrinsic relaxation time agrees reasonably well with the Debye-model calculations of Yafet. In our samples the probability of relaxation per surface collision for an electron spin is on the order of $10^{-3}$.

## I. INTRODUCTION

The temperature dependence of the conduction-electron-spin-resonance (CESR) relaxation time $T_1$ in sodium metal has sporadically been the subject of investigation for almost 20 years. A review of the theory and a rough calculation of $T_1$ based on the Debye model of the phonons has been given by Yafet,[1] and several experiments[2-4] agree well among themselves down to about 30 K. The temperature region below 30 K presents many obstacles to believable measurements, however, and even in the liquid-hydrogen temperature region (14–20 K), where the relaxation rate is not yet varying nearly as rapidly as the ultimate $T^5$ expected by Yafet, there are so many factors ignored by previous workers that it is difficult to have confidence in the results.

The only measurements undertaken so far measure $T_1$ by measuring $T_2$, the inverse linewidth in a cw experiment, on the grounds that even at microwave frequencies the complete-motional-narrowing condition $\omega_0 \tau \lesssim 1$ is satisfied, so that $T_1 = T_2$. In practice, of course, in the hydrogen-temperature region, and at $X$-band microwave frequencies, $\omega_0 \tau \sim 1$, and there *are* mechanisms that can cause $T_2$ to be less than $T_1$, and can also distort the line shape from the Lorentzian or the Dyson shape of the classical electron gas. Two such mechanisms have been reported by Schultz[5,6] and co-workers. One is the spin-wave sidebands which visibly distort the line even in the hydrogen-temperature region,[5] and other is incomplete motional narrowing of the electron wave-vector-dependent $g$ shift.[6] Only the former is important for sodium, but the remnants of spin waves can be seen at 10 GHz and 3500 G up to 17 K in transmission experiments.[7] In any event, we have eliminated possible errors caused by high magnetic field by working at 10 MHz and sweeping magnetic field between 0 and 10 G.

Another source of difficulty which can influence the determination of the intrinsic relaxation time is surface relaxation. As pointed out by Walker,[8]

in a slab of thickness $L \ll \delta_{eff} = (\frac{2}{3} v_F \Lambda T_2)^{1/2}$, where $\Lambda$ is the electron mean free path and $v_F$ the Fermi velocity, the electron may make collisions with the surface at the rate $2 v_F \Lambda / 3L^2$. If $\epsilon$ is the fraction of the time that the spin flips upon surface collision the surface relaxation rate is, by this crude argument,

$$1/T_s \cong \tfrac{2}{3} \epsilon \, v_F \Lambda / L^2.$$

One sees that even if $\epsilon$ is temperature independent, the electron mean free path $\Lambda$ is not, so that the measured surface relaxation rate has the temperature dependence of the electrical conductivity. Thus, the practice of measuring $T_2^{-1}$ at 4.2 K and using that value as the sum of impurity and surface relaxation rates with which to correct the liquid-hydrogen-region data is not valid.

However, the dependence of $T_s^{-1}$ on $L^{-2}$ provides the signature of $T_s$ so that, by using several samples of different thicknesses $L$, one can separate the surface contribution from the impurity and intrinsic rates, and at the same time, if $\Lambda$ is known, one can extract the surface spin-flip probability $\epsilon$.

The above remarks, then, define the program of the measurement: low frequencies and samples of different thicknesses. A more complete overview of the theory of the measurement is presented in Sec. II, followed by experimental details (Sec. III), and a concluding section (Sec. IV) containing results.

## II. PRINCIPLE OF THE MEASUREMENT

The inverse linewidth of the CESR, proportional to $T_2$, was measured by fitting the shape of the resonance line to the expression given by Lampe and Platzman[9] (LP), who give the absorbed power $P$ as

$$P = K \left[ \mathrm{Re} \left( Z_0^2 \, \frac{\cot 2W}{W} \right) \right], \tag{1}$$

where

$$W^2 = \tfrac{1}{2} a^2 [ i(\omega - \omega_0) T_2 - 1],$$

$$a^2 = L^2 / 4 \delta_{eff}^2,$$

$$K = |H_1(0)|^2 \frac{c^4}{(4\pi)^2} \left(2 \frac{T_2}{L}\right) a^2 \left(\frac{\omega_0}{\omega}\right) \chi_0 ;$$

$L$ is the thickness of the sample, $\delta_{eff}$ is the diffusion length of the conduction electrons in time $T_2$ (defined in Sec. I), and $Z_0$ is the sample-surface impedance. The formula is the one from Lampe and Platzman[9] appropriate to two-sided excitation of a slab of thickness $L$. Walker[8] has shown that Eq. (1) is valid at least for $L \ll \delta_{eff}$, because certain errors made by Dyson,[10] Kaplan,[11] and Lampe and Platzman,[9] all of whom solved the same problem in various ways, are exactly compensating.

The advantage of the LP approach is that they demonstrate the validity of their formula for arbitrary surface impedance $Z_0$ as long as the skin depth is much smaller than $\delta_{eff}$. That inequality is well satisfied in this measurement since the skin depth is a few microns, and $\delta_{eff}$ is always greater than 1000 $\mu$m. The validity of Eq. (1) for arbitrary $Z_0$ is essential, since for the hydrogen temperature range in sodium the surface impedance is neither in the classical nor the anomalous limits. But we do not need to know $Z_0$; we simply fit the data with the admixture of the real and imaginary parts of (cot$2W$)/$W$ as a free parameter.

Equation (1) is valid at high field and conditions of no saturation of the conduction electrons. As explained in Sec. I, our measurement is made at an rf frequency $\omega/2\pi = 10$ MHz, and the magnetic field $H_0$ is swept, in practice, from 2.54 to 5.10 G, with the field for resonance occurring at 3.57 G. There are two consequences of these experimental conditions which must be investigated before Eq. (1) can be accepted as adequate for our experiment. One is that since a linearly polarized rf field was used, the counter-rotating component cannot be ignored. The other is that the fractional change in absorbed power at resonance is on the order of 100 times smaller at 10 MHz than at 10 GHz. To observe the resonance at all it was necessary to use as large as possible an rf field amplitude, which appears as $|H_1(0)|^2$ in the prefactor $K$ of Eq. (1). The possibility of consequent saturation cannot be ignored.

We have solved the LP line shape for a linearly polarized rf field, including the necessary assumption that the conduction electron magnetization relaxes towards the instantaneous applied magnetic field. The details are given by Wang.[12] Briefly, we find that the quantity $\chi_0 \omega_0 T_2$ in the prefactor of Eq. (1) must be replaced by $\chi_0 \omega_0 T_2 + i\chi_0$. The result is simply to admix into the real part of $Z_0^2 \cot(2W)/W$ the imaginary part of that quantity with amplitude, relative to unity, of $-1/\omega_0 T_2$. Since the line is fit with the relative admixtures of the real and imaginary parts as a free parameter, the resultant line-shape modification is not

detectable expect to the extent that $|1/\omega_0 T_2|$ varies across the resonance line. In practice, the variation is from about $\frac{1}{23}$ to $\frac{1}{27}$, so the effect can be neglected.

As expected from Eq. (1), the signal is a strong function of rf power, and our ability to observe the resonance at all depends on our capacity to apply a large rf field. Although we have not solved the problem for arbitrary $H_1$, it is not unreasonable to suppose that for values of $H_1$ not outlandishly large, the effect on the line is to broaden it in the same way as a Lorentz line is broadened:

$$\Delta H = (1/\gamma T_2)(1 + \tfrac{1}{2}S), \tag{2}$$

where $\Delta H$ is the full width at half-maximum, $\gamma$ is the electron gyromagnetic ratio, and $S = \gamma^2 H_1^2 T_2^2$ is the saturation factor. The rf field amplitude was taken to be the surface field $H_1(0)$ reduced by the fraction of time that the electron spends in the skin depth:

$$H_1 = H_1(0)\, \delta/L. \tag{3}$$

Consequently, the effect of saturation is to broaden the line with an additional mechanism

$$(1/T_2)_{sat} = \tfrac{1}{2} S_0 (\delta^2/T_2)\, 1/L^2, \tag{4}$$

where $S_0 = \gamma^2 H_1(0)^2 T_2^2$ and $T_2$ is the total transverse relaxation time as measured. The form of Eq. (4) is convenient, since it has the same dependence on $L$ as the surface-relaxation term. Since we extract the surface-relaxation term from the experiments by plotting $T_2^{-1}$ vs $L^{-2}$, we can determine whether or not saturation is a serious problem by comparing an estimate of the coefficient of $L^{-2}$ with the measured slope of the $T_2^{-1}$-vs-$L^{-2}$ graphs. We find that with the realistic estimate of $H_1(0)$ equalling 0.5 G, the coefficient of $L^{-2}$ in Eq. (4) is never more than 5% of the smallest slope among the $T_2^{-1}$-vs-$L^{-2}$ graphs. Hence we believe that saturation broadening does not make a measureable contribution to our data.

There are three independent contributions to the spin-lattice relaxation time: surface relaxation, electron-phonon scattering with spin flip ("intrinsic"), and electron-impurity scattering with spin flip:

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{surf} + \left(\frac{1}{T_1}\right)_{int} + \left(\frac{1}{T_1}\right)_{imp}. \tag{5}$$

Only the impurity mechanism is temperature independent. The form of surface-relaxation term has been investigated by Walker.[8] He gives the surface contribution

$$(1/T_1)_{surf} = [\epsilon(1 + B_0)/(1 - \epsilon)]\, 1/\tau, \tag{6}$$

where $\epsilon$ is probability of a spin flip per electron encounter with the surface and $B_0$ is the first Lan-

dau Fermi-liquid parameter. If the sample thickness $L$ is small compared to the electron mean free path, then $(1/\tau) = (v_F/L)$, where $v_F$ is the Fermi velocity. In our case the electron mean free path is much smaller than $L$ except perhaps for the liquid-He data on some of the thinner samples. However, the diffusion length in $T_2$, $\delta_{eff}$, is much larger than $L$, so Eq. (6) is valid, with $\tau$ replaced by the diffusion time across the sample thickness $L$: $\tau_D = 3L^2/2v_F\Lambda$. Thus, Eq. (6) becomes

$$\left(\frac{1}{T_1}\right)_{surf} = \frac{\epsilon}{1-\epsilon}(1+B_0)\frac{2}{3}\frac{v_F\Lambda}{L^2} \cong \frac{0.5\epsilon v_F\Lambda}{L^2} \quad .$$
(7)

The approximate coefficient 0.5 appears because where we have chosen $B_0$ to be about $-0.25$, and assumed $\epsilon \ll 1$.

The object of the experiment is to determine the temperature-dependent intrinsic relaxation rate $(T_1)_{int}^{-1}$. If one plots the observed $T_2^{-1}$ at temperature $T$ in several samples of different thicknesses $L$ vs $1/L^2$, the result should be a straight line with slope $0.5\,\epsilon v_F\Lambda$. The line will be straight only if $\epsilon$ is constant from sample to sample. Assuming this turns out to be the case, the intercept at $L^{-2} = 0$ is $(T_2)_{int}^{-1} + (T_2)_{imp}^{-1}$. At 4 K, the intrinsic rate should be unobservably small, so that 4-K relaxation rate is determined only by surface relaxation and by impurities. Knowing the slope of $(T_2)^{-1}$ vs $1/L^2$ in the hydrogen range, plus the ratio of the electrical resistance of the sample at 4 K to, say, 20 K, and assuming $\epsilon$ is temperature independent, one can eliminate $(T_2)_{surf}^{-1}$ at 4 K, leaving only the temperature-independent impurity mechanism. In this way both surface and impurity contributions to the observed $T_2$ in the hydrogen range may be separated out, and the intrinsic relaxation rate deduced.

### III. EXPERIMENTAL DETAILS

#### A. Samples

The sodium samples were obtained from Taylor at Livermore. The quantity supplied was very large, and it was necessary to transfer the sodium to smaller vessels in order to be able to make samples. The original transfer of a rather small quantity of the metal was apparently of reasonable success in preserving the initial purity, but evidently the transfer (by melting) contaminated the remaining sodium, because when the quantity originally transferred (called group I in the data) became nearly depleted, a second transfer yielded samples (group II) that gave erratic and inferior results. The rest of the data (group III) were taken on the small piece of metal remaining from the original transfer, but the lapse of a year and the need to use metal near the edges of the piece as well as from the center evidently caused greater

variation in impurity content, so the data were treated separately. Samples, also originally from Livermore, were obtained from Cornell and Bell Laboratories, and proved to be of much lower quality than the samples we had been using.

The sodium was stored and cut to sample size under degassed deactivated Nujol. Slabs of sodium on the order of 1–2 mm thick were rolled to final sample thickness between two sheets of polyethylene with a small hand-cranked rolling mill, trimmed to final dimensions of about $1\times 0.5\times L$ cm, and inserted into a sample coil of 40 turns of No. 36 enamel-coated copper wire. The coil had been shaped to internal dimensions just slightly larger than the sample, and after the sample was inserted the coil was pinched gently against the sample in order to increase filling factor. The assembly, still coated with Nujol, was attached to the end of the coaxial down tube, a vacuum-tight can soldered around the assembly, evacuated, and cooled to 77 K as quickly as possible.

#### B. Electronic Apparatus

The resonance signals were observed with a hybrid-tee or bridge system very similar to the standard "magic-tee" apparatus used in microwave spectroscopy. The bridge was operated completely balanced, so that the resonance signal appeared as an imbalance voltage at the fourth arm of the tee. It was then amplified, and mixed with an rf reference signal whose phase was chosen to maximize the signal to noise.

The magnetic field was provided by a set of two concentric Helmholtz pairs, one of which was kept at a fixed field, and the other was swept from 0 to 2.56 G by a current derived from the analog sweep voltage of a Fabritek 1070 signal averager. The field was also modulated at 150 Hz, so that the signal from the rf phase-sensitive detector (rf mixer) was detected again with a PAR-122 lock-in amplifier. The output of the lock-in was stored in the signal averager, the analog sweep output of which provided the slow sweep of the field. A typical "pass" lasted 51.2 sec, during which the hybrid bridge usually remained well balanced, then the bridge was rebalanced if necessary and another pass stored. A run at a particular temperature consists of 4 to 16 passes. The data from a particular run, recorded on an $x$-$y$ recorder, are shown on Fig. 1.

#### C. Analysis of Data

The data stored in the signal averager were read out onto paper tape via a PDP-8/I computer for later analysis. The analysis consisted of fitting Eq. (1) to the experimental line shape by generating the theoretical shape with the PDP-8/I and superimposing the experimental and theoretical

TABLE I. Slope and intercept versus temperature (from the lines in group I of Fig. 1).

| $T$ | | | 20.2 °K | 17.0 °K | 14.1 °K | 4.2 °K |
|---|---|---|---|---|---|---|
| $m = 0.5$ $\epsilon$ $V_F$ $\Lambda$ | | | $64 \pm 10$ | $144 \pm 15$ | $190 \pm 15$ | $213 \pm 20$ |
| $(T_2)^{-1}$ intr. + imp. | (in $10^6$ sec$^{-1}$) | | $2.48 \pm 0.02$ | $1.98 \pm 0.02$ | $1.72 \pm 0.03$ | $1.42 \pm 0.10$ |
| $(T_2)$ intr. + imp. | (in $10^{-7}$ sec) | | $4.0 \pm 0.03$ | $5.1 \pm 0.07$ | $5.8 \pm 0.10$ | $7.0 \pm 0.05$ |

lines by eye using the scope display of the 1070 signal averager. The parameters varied to obtain the best visual fit were the desired quantity $T_2$; the admixture of real and imaginary parts of the line shape; the ratio of $\delta_{eff}/L$, to which the line shape was completely insensitive as long as $\delta_{eff} > 1$; and the height of the curve. The smooth solid line in Fig. 1 shows a typical fit achieved by this method.

The $T_2^{-1}$ values for the various samples are plotted vs $1/L^2$ in Fig. 2. The slopes, $m = 0.5 \epsilon v_F \Lambda$, intercepts $T_2^{-1}$, and $T_2$ are listed in Table I for the temperatures used in the experiment. The values are for group-I data; we believe that Fig. 2 shows that the group-III samples tended to be in agreement with group-I data but show substantially greater scatter.

An early measurement in our laboratory of the resistivity ratio of the bulk sodium from which group-I samples were taken gave $\rho(293 \text{ K})/\rho(4.2 \text{ K}) \cong 4000$.[7] We realize it is by no means obvious that, even if this ratio persisted in the actual samples used, we can assume that the mean free path in our samples is the same in, say, the hydrogen temperature range as other samples with the same resistance ratio. Lacking resistivity measurements in the hydrogen range, we can take the data analysis a step farther if we *do* assume that the mean free paths in the hydrogen range and at 4.2 K published by MacDonald[13] for a sodium sample with resistance ratio at 4000 are characteristic
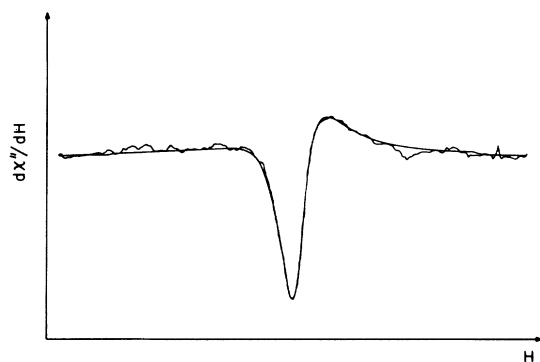
of our samples also. The values of $\epsilon = 2m/v_F \Lambda(T)$ and $\Lambda(T)$ from MacDonald are listed in Table II. We note that $\epsilon$ is gratifyingly a near constant in the hydrogen range. It would be tempting to assign the observed differences at the various temperatures to some true temperature dependence of the surface relaxation caused, perhaps, by surface phonon modes, but the uncertainties of the data and the remote origin of the mean-free-path data on which $\epsilon$ depends surely do not allow the possibility seriously to be entertained. Also, the small value of $\epsilon$ at 4.2 K is probably not significant for the following reasons. The signal to noise at 4.2 K was uniformly poor—data at the larger values of $L$ particularly is lacking. The mean free path of 130 $\mu$m at 4.2 K means that the sample thickness was not much larger than $\Lambda$, so that the surface relaxation term in equations was tending toward the temperature-independent ballistic $1/L$ limit rather than showing the diffusive temperature-dependent $1/L^2$ behavior.

Figure 3 is a plot of the relaxation rates with the surface relaxation mechanism removed (Table I) versus temperature. $T_2$ vs $T$ is plotted on a log-log plot in Fig. 4, along with the data of Kolbe.[14] The intrinsic relaxation times plotted there were obtained by assuming that the relaxation rate at 4.2 K was, in the limit of vanishing $1/L^2$, determined entirely by impurities. The straight line labeled "theory" was obtained from Fig. 2 of Kolbe,[14] who extended Yafet's[1] calculations through the hydrogen range using Debye temperatures for the normal and umklapp processes of 250 and 150 K, respectively.

Our results in the hydrogen range are in fact remarkably similar to Kolbe's[14] although he ignored surface relaxation, thus implicitly treating it as a temperature-independent process, and worked at a magnetic field high enough (8 kG) so that with his sample-purity spin-wave effects could have caused



FIG. 1. Data and typical fit to LP line shape (smooth curve). Magnetic field runs between 2.54 and 5.10 G, and $T_2 = 0.4 \times 10^{-6}$ sec for this example.

TABLE II. $\Lambda$ and $\epsilon$ versus temperature.

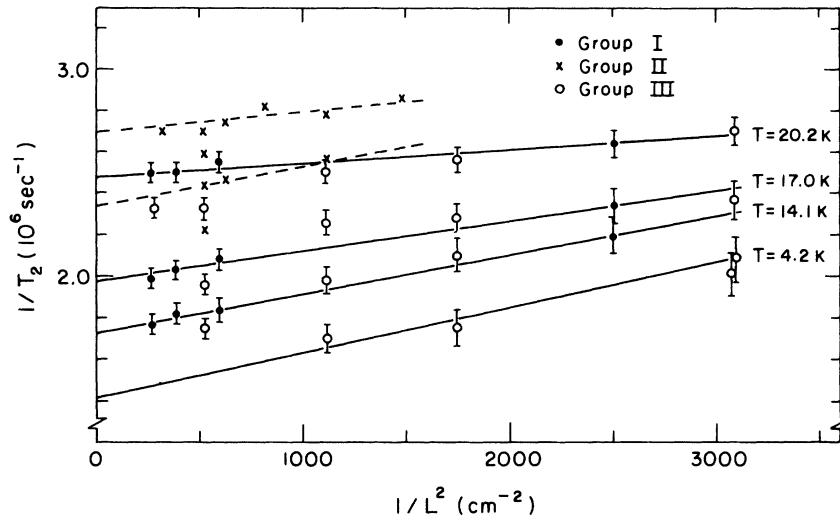| $T$ | 20.2 K | 17.0 K | 14.1 K | 4.2 K |
|---|---|---|---|---|
| $\Lambda^a$ | 8.5 $\mu$m | 17 $\mu$m | 40 $\mu$m | 13 $\mu$m |
| $\epsilon$ | $1.5 \times 10^{-3}$ | $1.7 \times 10^{-3}$ | $1 \times 10^{-3}$ | $0.3 \times 10^{-3}$ |

aReference 13.

FIG. 2. $T_2^{-1}$ vs $L^{-2}$ for all the data. Solid circles, group-I samples; crosses, group II; open circles, group III.

distortion of the resonance line. Since his samples were 100 $\mu$m thick, one can only conclude on the basis of our experience that surface relaxation in his samples was negligible.

At the frequencies used by Kolbe (24 GHz), the quantity $\omega_c \tau$ ranges from 1 to 3 in the hydrogen range, and is perhaps 20 at 4.2 K (using Mac-Donald's mean free paths), so the diffusion constant even in the hydrogen range is not isotropic, and our analysis would not be directly and easily applicable to his data. In particular, if the 4.2-K data were taken with the static magnetic field parallel to the surface, diffusion perpendicular to the plane of the sample would be relatively restricted, and surface relaxation quite possibly impeded. Unfortunately, it is not clear from Kolbe's paper what geometry was actually used in the experiment, since both geometries were allowed by

the geometry of the apparatus.

## IV. SUMMARY

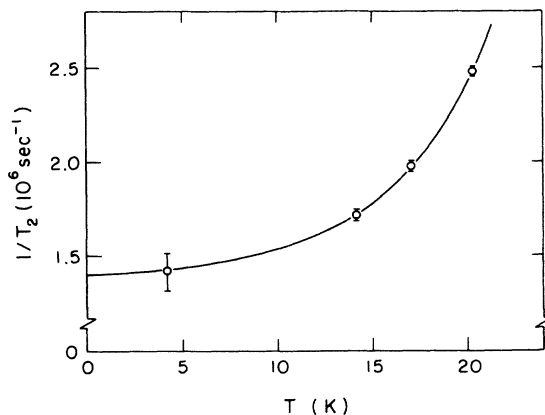By working with sodium samples of homogeneous origin, at low magnetic fields, and prepared with

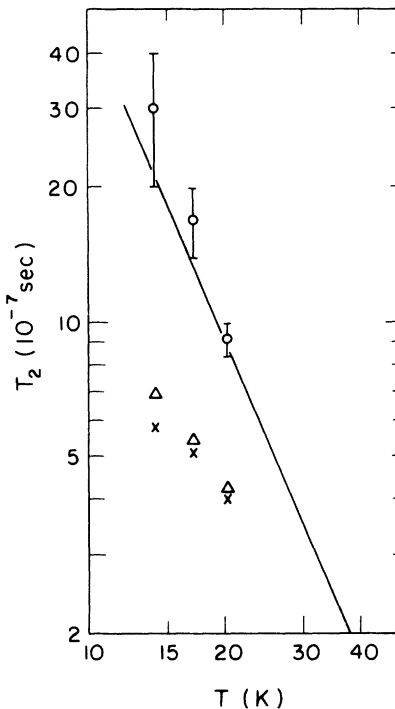FIG. 3. Relaxation rates with surface relaxation removed vs $T$.

FIG. 4. Relaxation times vs temperature. Crosses, $T_2$ intrinsic plus impurity; open circles, $T_2$ intrinsic; triangles, $T_2$ from Kolbe (Ref. 14), including impurity and surface relaxation; solid line, Yafet's calculated curve (after Kolbe).

controlled geometry, we have isolated the surface relaxation contribution to the measured relaxation time $T_2$ in the liquid-hydrogen temperature region. It is explicitly illustrated that even if the spin-flip probability per surface collision is temperature independent, the surface contribution to the total relaxation rate in thin slabs is temperature dependent, since the rate at which surface collisions occur depends on the electron mean free path, a temperature-dependent quantity. Within the limitations of experimental accuracy, we find that the probability of relaxation of an electron per surface collision $\epsilon$ is on the order of $10^{-3}$, and is temperature independent in the hydrogen temperature range.

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