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Electron Spin Resonance Absorption in Metals. I. Experimental

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The electron spin resonance absorption in metals was investigated at 300 and 9000 Mc/sec, in the temperature range from 4°K to 296°K. The metals investigated were: Li, Na, K, Be, Mg, Al, Pd, W. Resonances were observed in Li, Na, Be, for which accurate g values and relaxation times were obtained and compared with existing theories. K gave a signal only at 4°K and 300 Mc/sec, with too poor a signal-to-noise ratio to make accurate measurements. No resonances were observed in Mg, Al, Pd, W. The line shapes predicted by Dyson's theory for the resonance absorption in metals were checked experimentally for different diffusion times and relaxation times. A satisfactory agreement between the theory and experiment is obtained for both the normal and the anomalous skin effect region.

I. INTRODUCTION

THE first paramagnetic resonance absorption in metals due to conduction electrons was observed by Griswold, Kip, and Kittel.[1] At that time there was no theory to take the diffusion of the electrons properly into account and therefore exact g values and relaxation times could not be obtained. The purpose of this paper is to report on the extension of the work on electron spin resonance absorption in metals, making use of Dyson's theory (see following paper) on line shapes. With its aid accurate g shifts and relaxation times were obtained and are compared with existing theories.

II. THE EXPERIMENTAL SET-UP

Most of the experiments were performed at 300 megacycles per second. A block diagram of the experimental arrangement is shown in Fig. 1. The heart of the setup is a coaxial resonant cavity, which is one-half wavelength long and has a Q of about 1000–2000. The same cavity may be used at a frequency of 600 and 900 megacycles per second, in which case it will be a full wavelength or $\frac{3}{2}$ wavelength long. In either case it is used as a transmission cavity. The power is fed in and taken out by two identical coupling loops. Their length and orientation may be changed from outside to give optimum coupling conditions, which may be measured by means of the voltage standing wave ratio. Line stretchers are used for matching purposes.

The output of the cavity is rectified by means of a grid leak detector, which proved to be much less noisy than a crystal rectifier. The detector output feeds into a 6-kilocycle-per-second narrow-band amplifier. It has a Q of 85, maximum amplification of 120 db and an equivalent noise input voltage of 0.05 microvolt. It is followed by a lock-in detector which further cuts down the band width and hence the total amount of noise power coming through. Its output contains the desired signal and can be displayed either on a scope or Brown Recorder.

The magnetic field is obtained from a water-cooled solenoid (50 cm long) with an inner diameter of 6 cm. To improve on the uniformity of the field, compensating coils are wound on each end of the solenoid. This reduces the field variations to about one part in 10^5 for the central 10 cm of the solenoid. The magnetic field for a power input of 1.5 kw is 1000 oersteds, which is the maximum safe field to be used.

The dc magnetic field is modulated at a rate of six kc/sec by means of an auxiliary winding. Since the modulation is always small in comparison to the line width, the observed signal is proportional to the derivative of the absorption. The modulating coil is not wound along the entire length of the dc windings. This reduces the coupling between the two coils and hence reduces the shorting effect of the dc winding. To prevent the resonant cavity from acting as a shorted turn for the six kc/sec, it is provided with a longitudinal slot. Such a slot runs parallel to the rf currents in the cavity and therefore does not lower noticeably the Q of the cavity.

The dc field may be slowly varied by means of a motor driven rheostat. Unfortunately the variable contact resistance of the rheostat causes current fluctuations (and hence corresponding field fluctuations) of approximately one part in 10^4. Thus for narrow lines (of the order of 0.1 oersted) an alternate method of sweep was developed. It consists of a copper coil in an oil bath whose temperature may be either increased or decreased by means of a heating coil or water cooling system, respectively. As the temperature changes, the resistance of the coil changes and the current through the magnet varies. By this method a smooth variation of 10 percent of the current is easily attained. At 300 Mc/sec this corresponds to about 10 oersteds.

The magnetic field can be determined to an accuracy of one part in 10^5 by means of a standard resistor and potentiometer. The frequency is determined by means of a frequency meter to three parts in 10^5. This limits the accuracy with which the g values of the electrons in the investigated material may be determined. For broad lines an additional error is introduced in locating the exact resonance condition on the line. For those lines a 3-cm setup, having a higher dc field, is better suited for

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[1] Griswold, Kip, and Kittel, Phys. Rev. 88, 951 (1952).

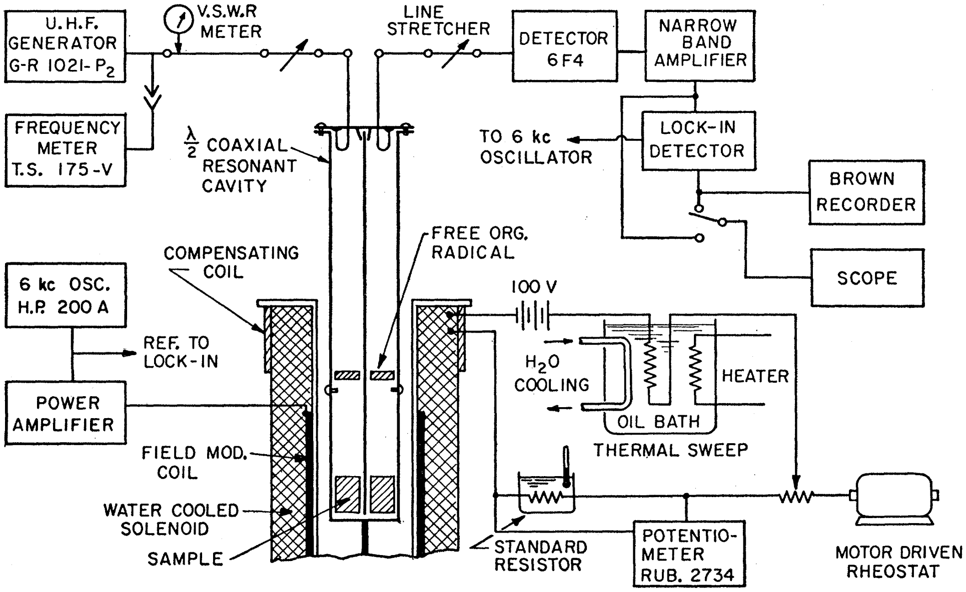

FIG. 1. Experimental setup for electron spin resonance absorption at 300 Mc/sec.

exact g determinations and was used by us for this purpose.

For the absolute measurement of susceptibilities, and for general calibration purposes a known amount of an organic free radical (diphenyl picryl hydrazyl) is placed in the cavity simultaneously with the sample. The position of the free radical sample is such that it sees a lower rf field, lower dc magnetic field and a lower modulation field. The reason for choosing its position in this way is as follows: it prevents the free radical absorption from falling on top of the investigated lines, which almost invariably are located around $g=2.00$. The different dc magnetic field displaces it sufficiently to avoid any interference. (See Fig. 9.) Most lines investigated have broader lines than the diphenyl picryl hydrazyl (which, depending on the temperature, has a width of approximately one to two oersteds between inflection points). Thus for a proper sample modulation, the free radical would be overmodulated. The fact that it is located in a weaker rf magnetic field makes it a valuable reference for saturation measurements where rf fields of the order of oersteds may have to be used.

In order to cool the sample to below room temperature, two coaxial Dewars are used. Into the inner one the cavity is suspended by two coaxial lines (input and output) whose inner and outer conductors are made out of brass to reduce the heat loss by conduction.

The range between liquid nitrogen (77°K) and room temperature is covered by filling the space between the two Dewars with liquid nitrogen and mounting a heater in thermal contact with the cavity. By adjusting the power input to the heater, any equilibrium temperature within the above range may be obtained and kept constant to a fraction of a degree. In order to prevent the condensation of oxygen below 90°K, the inner Dewar in which the cavity is situated is made vacuum tight and filled with helium gas.

The temperature range between 4°K, and 77°K, is covered by mounting a brass rod at the end of the cavity. The temperature of the cavity will then be determined by the position of the liquid-helium level on the brass rod. In order to avoid temperature changes while sweeping through a line, parts of the brass rods are thermally "shorted out" by copper blocks. Since the thermal conductivity of copper at 4°K is about one hundred times higher than that of brass, no appreciable difference in temperature occurs while the helium is in contact with the copper blocks. This method works only if the rate of evaporation is low. If this is not the case, the helium vapor rather than the brass rods will be effective in cooling the cavity. The rate of loss of liquid helium without any rf in our system is 30 cc/hour which corresponds to about 25 mW. Since the rf powers ordinarily used are of the same order, an improvement of the Dewar design would not result in an appreciably lower rate of helium loss. Incidentally, a measurement of the loaded and unloaded Q of the cavity, together with the rate of helium evaporation, may be used to calculate the rf magnetic field in the cavity. This is an important quantity for saturation measurements.

It was found that when the cavity is filled with liquid helium, the noise output increases greatly. This extra noise source was attributed to bouncing helium bubbles within the cavity. In order to eliminate this trouble, the entire cavity is filled with Styrofoam, a low-loss material with a dielectric constant of 1.0.

The temperatures are read with an AgAu-AuCo thermocouple, which, unlike most other thermocouples, is still useful in the 4°K range. At this temperature it has a slope of approximately five microvolts per degree. The thermocouple is soldered to the wall of the cavity at the place where the sample is situated.

The sensitivity of the 300-Mc equipment at room temperature, set by the random noise fluctuations, corresponds to about 10^{16} free electron spins having a line width of one oersted. A curious sensitivity limit for broad lines is set by what is loosely called cavity effects. Those are reproducible lines of several oersteds width and occur at different g-values. They probably are the result of impurity inclusions in the walls of the cavity. Since the occurrence of the peaks depends on the previous history of the magnetic field, they are presumably ferromagnetic inclusions. A more careful silver plating job probably would eliminate this trouble.

Let us consider now how the sensitivity changes on going from 300 Mc/sec (at which frequency most of this work was done) to 9000 Mc/sec, which is the more conventional frequency for electron spin resonance experiments. The higher fields which are used with higher frequencies give rise to a larger difference in population of spin states, and hence to a larger signal. However, for metal samples large compared to a skin depth, the effective volume of the sample goes down with increasing frequency (because of the skin depth), so that for a constant line width with comparable Q's and filling factors the fractional power absorbed at resonance

$$\Delta P_C/P_C \cong (\omega)^{\frac{1}{2}}.$$

This would indicate that the expected sensitivity at 9000 Mc/sec should be about 6 times better than at 300 Mc/sec. However, the crystal detectors used at microwave frequencies are much noisier than the vacuum tubes used at uhf frequencies, so that we get about equal sensitivities as far as metals are concerned.

The advantage of the lower frequency set-up was the homogeneity and stability of the magnetic field, which made it possible to investigate very narrow lines (e.g., sodium at 4°K). On the other hand, lines broader than 100 oersteds (the field at 300 Mc/sec) cannot be investigated profitably at 300 Mc/sec.

III. PREPARATION OF SAMPLES

The samples investigated were of two forms. Either their dimensions were small in comparison to a skin depth at 300 Mc/sec (i.e., thin films or dispersions of particles), or large in comparison to a skin depth (i.e., sheets or large particles).

For all metals except the alkalis, the sample had dimensions large in comparison to a skin depth. When particles were used, they were imbedded in paraffin and molded into the desired shape. When metal plates were used, they were sandwiched between polystyrene sheets in order to expose more sample volume to the rf field. In this case it is important to insert the metal plates into the cavity in such a way that the E field is perpendicular to the metal surface. This reduces the losses due to the sample.

Small particles of the alkalis were prepared by ultrasonerating the bulk metal in mineral oil at a frequency of 700 kc/sec. The average particle size of such a dispersion was $\sim 15\mu$. In order to obtain a dispersion with all particles smaller than a skin depth, the sample was centrifuged at $2000g$ for several hours which sedimented out the large particles. (For the experimental result on such a centrifuged dispersion, see Fig. 8.)

Sheets of the alkali metals were prepared by rolling out the bulk material in molten paraffin. Mineral oil was found to react with the metal to form free radicals which obscured the metallic resonance at low temperatures (see Sec. IV, A-2) and therefore was substituted by the molten paraffin. An alternate way of making thick sheets of Li and Na is to put the bulk metal between two sheets of Parafilm (a thin strengthened sheet of paraffin, commercially available from the Central Scientific Company) and roll it out on a regular sheet metal roll. This is a much faster method, but the samples have to be used within a few days since they are more likely to react in air.

Some alkali films (up to 0.15-mm thickness) were also evaporated in vacuum on thin mica sheets. Before exposing them to air, a thin protective layer of paraffin was evaporated onto them. The main purpose of this technique was to purify the metals. (See Sec. IV, C.) In the case of thin films this also provided the sample for the determination of the absolute value of the susceptibility.

During the writing of this paper some work performed with R. A. Levy indicates that when alkali metals are dissolved in ammonia, they precipitate out as metallic particles below the freezing point of ammonia ($\sim$190°K). This seems to be a promising way of preparing samples, especially of the more reactive alkalis.

IV. EXPERIMENTAL RESULTS AND THEIR COMPARISON WITH EXISTING THEORIES

A. Line Shapes in the Region of the Normal Skin Effect

1. Dyson's Theory

The references to Dyson's formulas in the following paper will be prefixed by *D*. Dyson treats the problem of electron diffusion in connection with the paramagnetic resonance in metals and obtains closed expressions for different experimental conditions. We will recapitulate briefly (in a slightly simplified form) some of his main results which are going to be used throughout this paper.

The main parameters in Dyson's theory are: T_D = time it takes an electron to diffuse through the skin depth; T_1 = electron spin relaxation time; (for metals $T_1 = T_2$); T_T = time it takes the electron to traverse the sample. The simplest case is:

$$T_T \ll T_D;$$

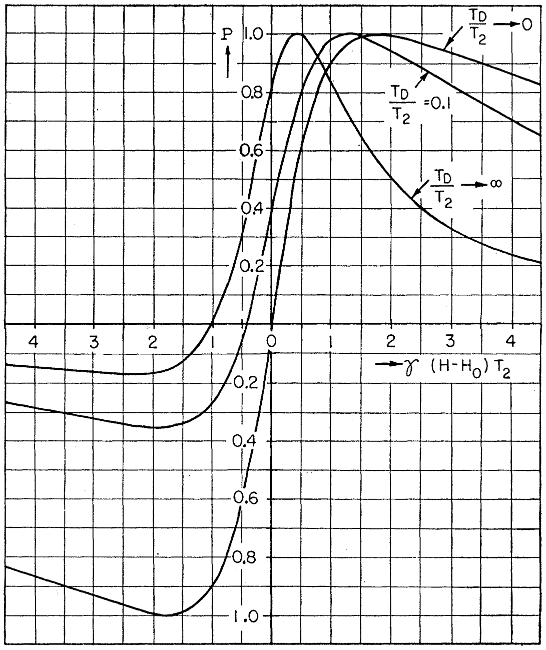

FIG. 2. Power absorption due to electron spin resonance in thick metal plates for different ratios of diffusion time T_D to relaxation time T_2.

i.e., a film (or particle) of thickness small in comparison to the skin depth. Under those conditions the power absorbed (D-78) is

$$P=\frac{\omega H_1^2}{4}(V)\omega_0\chi_0T_2\frac{1}{1+(\omega-\omega_0)^2T_2^2},\tag{3.1}$$

and the experimentally observed quantity is

$$\frac{dP}{d\omega}=-\frac{\omega H_1^2}{4}(V)\omega_0\chi_0T_2\frac{2(\omega-\omega_0)T_2^2}{[1+(\omega-\omega_0)^2T_2^2]^2},\tag{3.2}$$

where V = volume of the sample, H_1 = amplitude of the linearly polarized magnetic rf field, χ = paramagnetic part of the static susceptibility, and ω_0 = the resonant frequency satisfying the condition $\hbar\omega_0=g\beta H$.

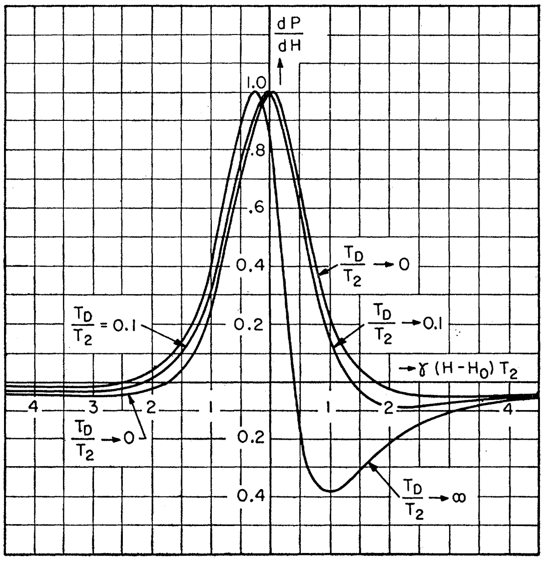

FIG. 3. Derivative of the power absorption due to electron spin resonance in thick metal plates for different ratios of diffusion time T_D to relaxation time T_2.

As expected, this result is entirely independent of diffusion and gives a symmetrical Lorentz line with the natural half-width $1/T_2$.

A more important case is:

$$T_T\gg T_D,\quad T_T\gg T_2.$$

This condition is always fulfilled for sufficiently thick samples. The general result for an arbitrary ratio of T_D/T_2 is (D-82):

$$\begin{aligned}P=-\left[\frac{\omega H_1^2}{4}(\delta A)\omega_0\chi_0T_2\right]\frac{T_D}{2T_2}\Bigg\{&\frac{R^4(x^2-1)+1-2R^2x}{[(R^2x-1)^2+R^4]^2}\\&\times\left[\frac{2\xi}{R(1+x^2)^{\frac{1}{2}}}+R^2(x+1)-3\right]\\&+\frac{2R^2-2xR^4}{[(R^2x-1)^2+R^4]^2}\\&\times\left[\frac{2\eta}{R(1+x^2)^{\frac{1}{2}}}+R^2(x-1)-3\right]\Bigg\},\end{aligned}\tag{3.3}$$

where $x=(\omega-\omega_0)T_2$, $\xi=(\text{sign of }x)[(1+x^2)^{\frac{1}{2}}-1]^{\frac{1}{2}}$, $\eta=[(1+x^2)^{\frac{1}{2}}+1]^{\frac{1}{2}}$, $R=(T_D/T_2)^{\frac{1}{2}}$, $\delta=c/(2\pi\sigma\omega)^{\frac{1}{2}}$ = classical skin depth, and A = area of surface.

Equation (3.3) is plotted in Fig. 2 for different ratios of T_D/T_2. The experimentally observed derivative of P with respect to H was taken graphically from plots of Eq. (3.3) or computed for the cases $T_D/T_2\ll1$; $T_D/T_2\rightarrow\infty$ for which asymptotic expressions were derived. They are plotted in Fig. 3.

Since those limiting cases are much easier to handle than Eq. (3.3) it seemed worthwhile to list them below.

(a) $T_T\gg T_D$; $T_T\gg T_2$; $T_D/T_2\rightarrow0$.

This condition applies to metals of high conductivity (low temperature) and narrow lines (D-88).

$$P\cong-\left[\frac{\omega H_1^2}{4}(\delta A)\omega_0\chi_0T_2\right]\left\{\left(\frac{T_D}{T_2}\right)^{\frac{1}{2}}\times\frac{[(1+x^2)^{\frac{1}{2}}-1]^{\frac{1}{2}}}{(1+x^2)^{\frac{1}{2}}}(\text{sign of }x)\right\},\tag{3.4}$$

$$\frac{dP}{d\omega}=-\left[\frac{\omega H_1^2}{4}(\delta A)\omega_0\chi_0T_2\right]\left\{\frac{T_2}{2}\left(\frac{T_D}{T_2}\right)^{\frac{1}{2}}\times\frac{[2-(1+x^2)^{\frac{1}{2}}][(1+x^2)^{\frac{1}{2}}+1]^{\frac{1}{2}}}{(1+x^2)^{\frac{3}{2}}}\right\}.\tag{3.5}$$

(b) $T_T\gg T_D$; $T_T\gg T_2$; $T_D/T_2\ll1$.

This case is similar to the preceding one except that we keep terms of the order T_D/T_2. Thus we have to add to Eq. (3.5) a correction term.

$$\frac{dP}{d\omega}=\text{Eq. (3.5)}-\left[\frac{\omega H_1^2}{4}(\delta A)\omega_0\chi_0 T_2\right.$$
$$\left.\times\left\{T_2\left(\frac{T_D}{T_2}\right)^{\frac{3}{2}}\frac{[(1+x^2)^{\frac{1}{2}}-1]^{\frac{1}{2}}}{(1+x^2)^{\frac{1}{2}}}\right\}.\qquad(3.6)$$

(c) $T_T\gg T_D;\quad T_T\gg T_2;\quad T_D/T_2\gg 1.$

This is again the thick-plate case with slowly diffusing magnetic dipoles. This case is well known from nuclear resonance in metals,[2] since the nuclei are almost completely stationary. This condition would also prevail in the case of paramagnetic impurities distributed throughout the volume of the metal. For these conditions we have: (D-84)

$$P=\left[\frac{\omega H_1^2}{4}(\delta A)\omega_0\chi_0 T_2\right]\left\{\left(\frac{1}{2}\right)\frac{1-T_2(\omega-\omega_0)}{1+T_2^2(\omega-\omega_0)^2}\right\},\qquad(3.7)$$

$$\frac{dP}{d\omega}=\left[\frac{\omega H_1^2}{4}(\delta A)\omega_0\chi_0 T_2\right.$$
$$\left.\times\left\{\left(\frac{T_2}{2}\right)\frac{T_2^2(\omega-\omega_0)^2-2T_2(\omega-\omega_0)-1}{[1+T_2^2(\omega-\omega_0)^2]^2}\right\}.\qquad(3.8)$$

All of the expressions (3.1) to (3.8) are only approximations to Dyson's formulas which include another term equal to the expressions themselves, but having $(\omega-\omega_0)$ replaced by $(\omega+\omega_0)$. (Note: ω_0 and H are freely interchanged in all the discussions, because of their relation: $\hbar\omega_0=g\beta H$, i.e., $\omega_0=\gamma H$.) For reasonably narrow lines this term may be neglected near a resonance. Physically this term arises from the use of a linearly polarized magnetic rf field, which is a superposition of two circularly polarized fields. One of them, having the same sense of rotation as the precession of the electron, is much more effective than the other in flipping the spins.

Another effect which is not included in expressions (3.1) to (3.8) is that of surface relaxations, which are important whenever there exist strong spin-dependent forces during a collision of the electron with the surface. Dyson treats this modification and shows that in the case of thin films or small particles one expects a much more marked effect than in the thick cases. From the experimental results, to be discussed in the next section, we can conclude that for the case of thick alkali metals this effect may be neglected.

Having a theory for the line shape, one may now proceed to extract the desired information from it.

Figures 4 and 5 show the point on the curve at which the resonance condition is satisfied for different ratios of T_D/T_2. This enables one to determine accurate g values.

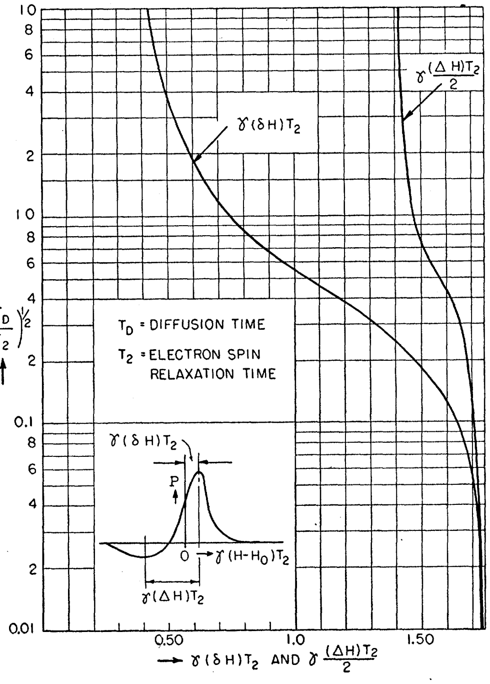

FIG. 4. $\gamma(\delta H)T_2$ and $\gamma(\Delta H)T_2/2$ vs $(T_D/T_2)^{\frac{1}{2}}$ for the power absorption due to electron spin resonance in thick metal plates.

They also show the way in which the half-power absorption points may be used to determlne the relaxation time T_2.

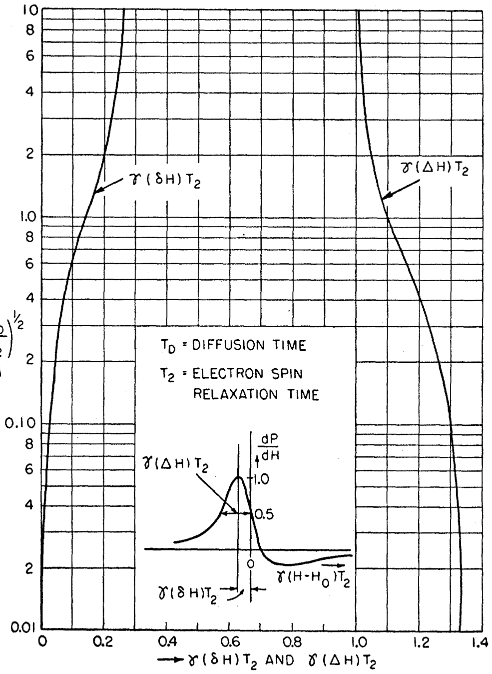

FIG. 5. $\gamma(\Delta H)T_2$ and $\gamma(\delta H)T_2$ vs $(T_D/T_2)^{\frac{1}{2}}$ for the derivative of the power absorption due to electron spin resonance in thick metal plates.

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[2] N. Bloembergen, J. Appl. Phys. 23, 1379 (1952).

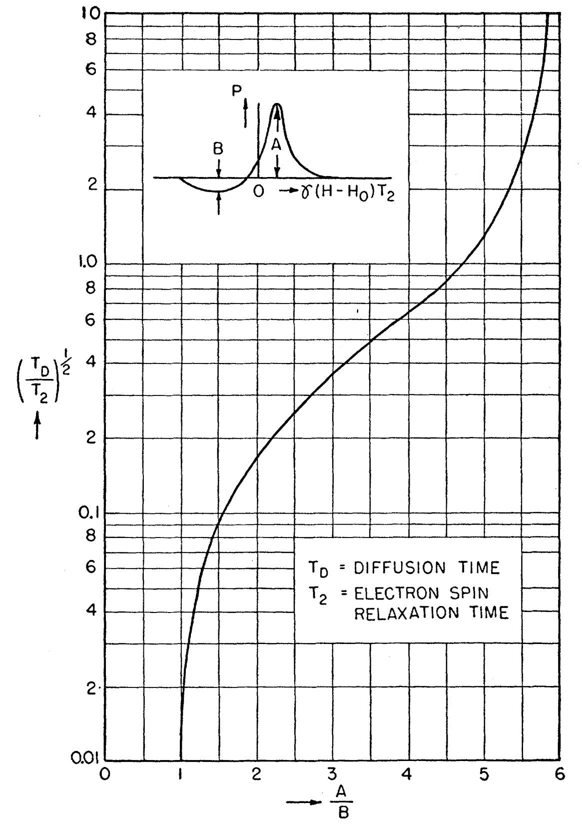

FIG. 6. A/B *vs* $(T_D/T_2)^{\frac{1}{2}}$ for the power absorption due to electron spin resonance in thick metal plates.

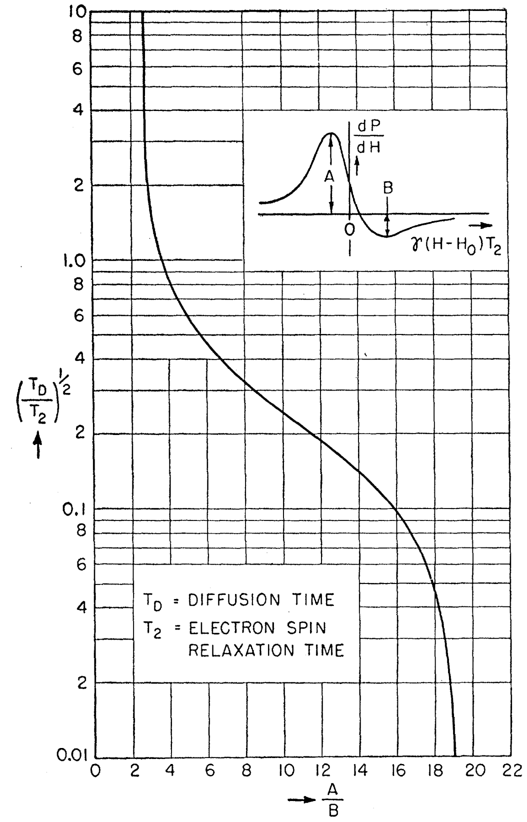

FIG. 7. A/B *vs* $(T_D/T_2)^{\frac{1}{2}}$ for the derivative of the power absorption due to electron spin resonance in thick metal plates.

Figures 6 and 7 show the changes in the asymmetry of the line when the ratio T_D/T_2 is varied. This is a convenient parameter to test the theory against experiment, as will be done in the next section.

2. Comparison of Dyson's Theory with Experiment

In order to determine to what extent surface relaxations are important, the line widths in dispersed sodium and lithium were compared with those in bulk samples (for the preparation techniques, see Sec. III). The particle size in all dispersions was smaller than 5μ, which is less than the skin depth at 320 Mc/sec. At $T=296°$K and $f=300$ Mc/sec the skin depth for Na is 6μ and for Li, 8μ. The theoretical expression is given for this case by Eq. (3.2). It is compared in Fig. 8 with the experimental curve obtained from a sodium dispersion with which it agrees very well. This confirms Dyson's assumption that the relaxation proceeds exponentially. From the curve we find a total relaxation time $T_2=6\times10^{-9}$ sec, as compared with the relaxation time in the bulk metal of $T_2=9\times10^{-9}$ sec. This discrepancy is within the variation of the relaxation times observed in different samples. But even if this difference were genuinely due to a surface phenomenon, it would lead to a surface relaxation time of 2×10^{-8}, which can be shown to have a negligible effect on the line shape in thick samples (see Appendix A) and will be henceforth neglected. Similarly it was found that surface relaxations could be neglected in bulk Li samples which had a relaxation time of 2×10^{-8} sec.

We proceed now to the more important case of thick plates. Figure 9 shows the experimental results in Li for different ratios of T_D/T_2. We see that as T_D/T_2 decreases, the sharp minimum of the derivative of the absorption disappears. Comparing the curves with Fig. 3, we see immediately the quantitative agreement with Dyson's theory.

The resistivity data which were used to calculate the diffusion time were taken from the work of MacDonald and Mendelssohn.[3] The Li used was obtained from the Lithium Corporation of America and was 99.9 percent pure; the sodium was obtained from A. D. MacKay Company and was 99.99 percent pure.

For a more quantitative test of Dyson's theory, the ratio between the maximum and minimum of the derivative of the absorption *vs* field was taken. This ratio A/B, according to Dyson's theory, should change from 2.7 to 19 over the entire range of T_D/T_2 (see Fig. 7). It

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[3] D. K. C. MacDonald and K. Mendelssohn, Proc. Roy. Soc. (London) **A202**, 103 (1950).

is a convenient parameter since it may be varied easily by changing the temperature of the sample.

Figure 10 shows the comparison between theory and experiment. It is seen that most of the experimental points lie to the left of the curve, indicating that the diffusion time of the electrons is longer than that calculated from the resistivity data. This could be explained under the assumption that surface irregularities impede the diffusion of the electrons into the metal and thus lengthen T_D. This assumption seems to be born out by a sodium sample which had an exceptionally smooth surface and lies very near the theoretical curve. It was prepared by pouring molten sodium under vacuum conditions into the space between two smooth concentric glass cylinders. The Be sample which had a shiny metallic surface lies also on the theoretical curve.

We may thus conclude that the agreement between Dyson's theory and experimental results on thick plates is satisfactory.

In this connection it should be noted that the proper value of the experimentally observed parameter A/B may always be taken as conclusive evidence that the absorption is due to diffusing electrons. By a careful determination of this ratio, one can find the diffusion time of the electrons. The theoretical expression for the diffusion time under the assumption that the mean free path Λ is small in comparison to a skin depth and

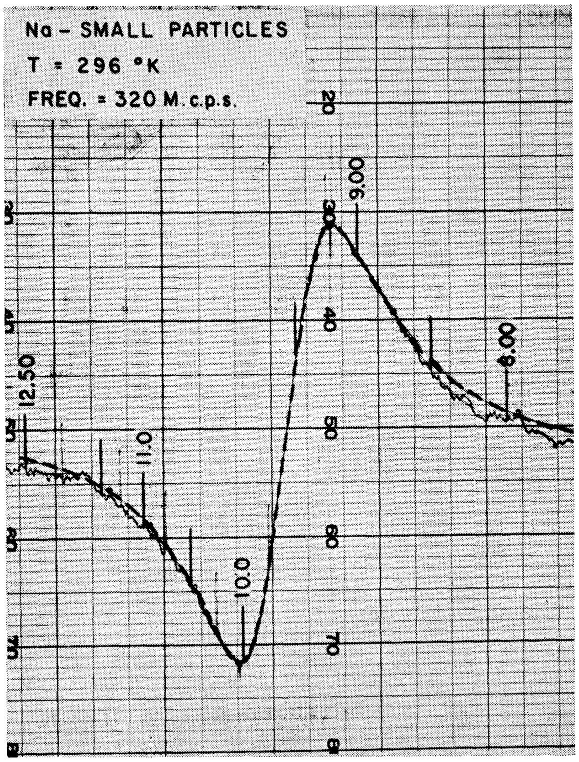
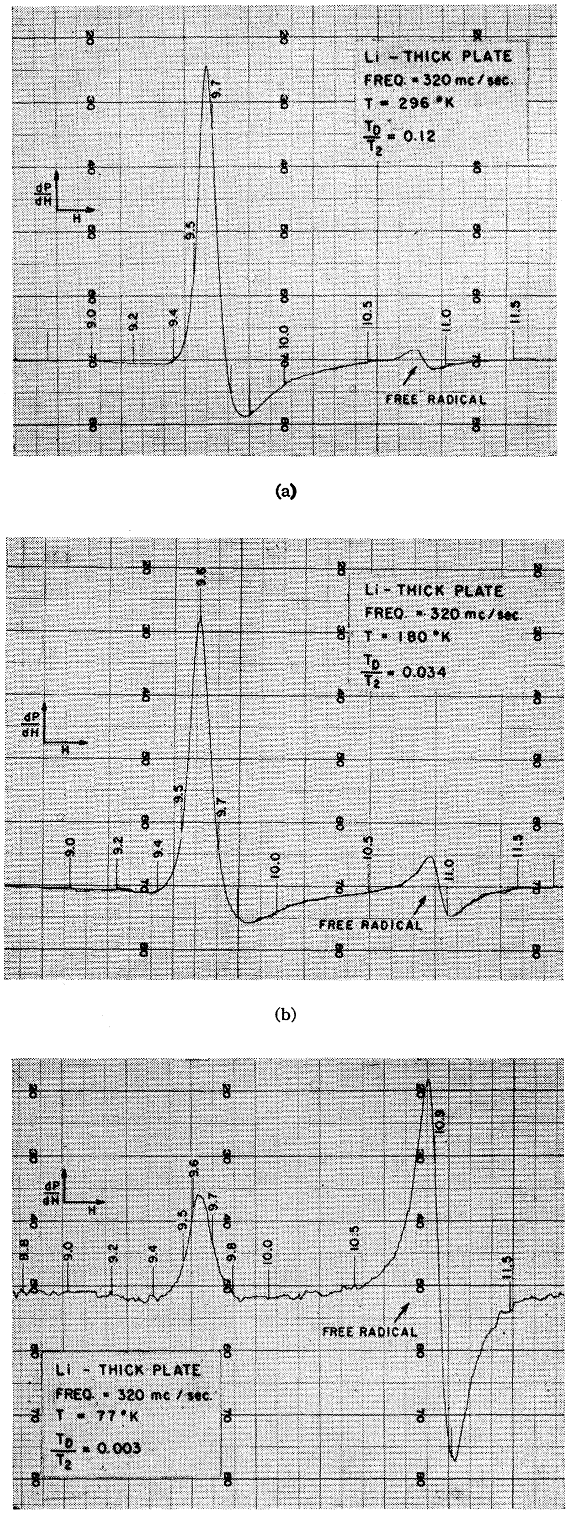


FIG. 8. Electron spin resonance absorption in small sodium particles. Diameter of particles smaller than 5 microns.



(a)

(b)

(c)

FIG. 9 (a, b, c). Electron spin resonance in thick plates of lithium for different ratios of T_D/T_2. Markers are proportional to the magnetic field. 1 unit = 11.77 oersteds. Compare the shape with the theoretical curves of Fig. 3.

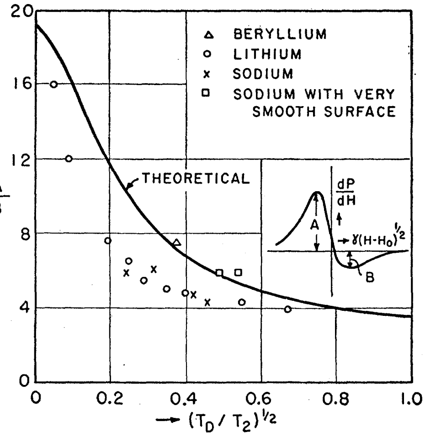


FIG. 10. Comparison of the asymmetry parameter A/B with theory for different ratios of T_D/T_2. The discrepancy is believed to be due to surface irregularities.

that all the electrons have the same velocity v is given by (D-11)

$$T_D=\tfrac{3}{2}(\delta^2/v\Lambda).$$

Eliminating Λ by means of the conductivity expression $\sigma=Ne^2\Lambda/m^*v$, we get

$$T_D=\tfrac{3}{2}(\delta^2Ne^2/\sigma)(1/m^*v^2).$$

Thus the experimentally measured quantity is proportional to $\frac{1}{2}m^*v^2$, which for a quadratic isotropic energy surface corresponds to the Fermi energy. From the observed ratio of A/B in beryllium we find that $\frac{1}{2}m^*v^2=16\pm2$ ev. The calculated value on a free electron model, taking $m^*/m=1$, gives a value of 14.3 ev. The closeness of the two values is rather surprising considering the crudeness of a free electron picture for beryllium.

Another importance of the parameter A/B lies in the fact that an undesired resonance due to impurities may be spotted immediately, since stationary paramagnetic impurities at the surface of the metal would give $A/B=1$; if they are distributed throughout the volume $A/B=2.7$ for a Lorentzian line and $A/B=2.0$ for a Gaussian line. The ratios 1 and 2.0 can never be due to conduction electrons in thick plates, whereas the ratio 2.7 could only occur in the limiting case of very slow diffusion and broad lines never observed in practice. This is a definite advantage of working with thick plates rather than small particles. In the latter case $A/B=1$, the same as for any kind of impurities. This can be very misleading (and did indeed mislead us for a while), especially when working with alkali metals. They form free radicals with mineral oil which at liquid helium temperature can completely obscure the metallic resonance (due to their $1/T$ dependence). Their line width is several oersteds at liquid helium temperature. Waxes which are solid at room temperature are much less troublesome in this respect. We found that the best of them comes under the trade name of "Parowax."

B. Line Shapes in the Region of the Anomalous Skin Effect

The expression for the classical skin depth is only valid when the mean free path Λ of the electrons in the metal is small in comparison to the skin depth δ. For the alkali metals at 300 mc, δ equals Λ at about 40°K, so that for the entire temperature region below liquid nitrogen the skin effect is partially or completely anomalous and must be handled by the exact theory of Reuter and Sondheimer.[4]

The Dyson theory was extended to the case of anomalous skin effect by Professor C. Kittel, and the resulting

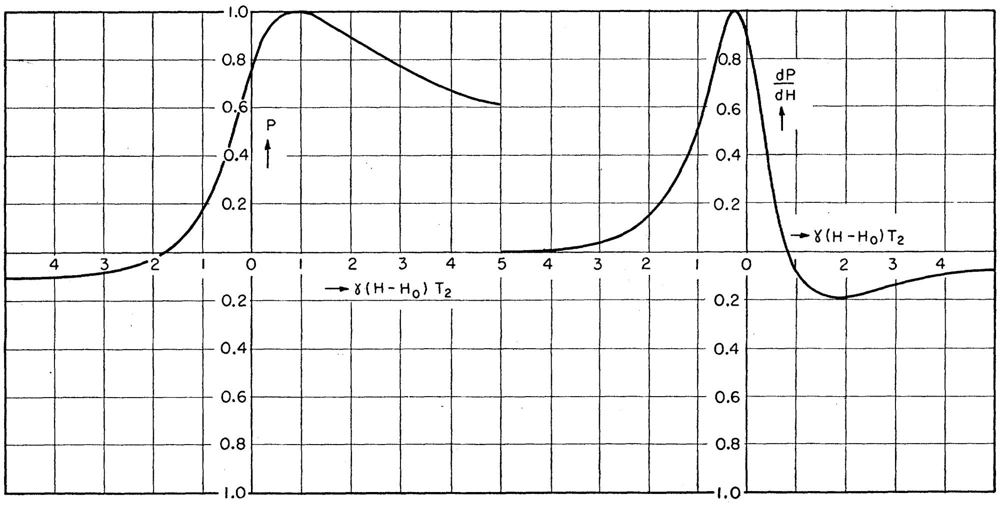


FIG. 11. Theoretical curves for the electron spin resonance absorption in the region of the completely anomalous skin effect.

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[4] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc (London) **A195**, 336 (1948).

line shape is given by Eqs. (D-26) and (D-40). The extended theory is valid only under the assumption that the diffusion time D is short in comparison to the relaxation time. This assumption is valid for all the metals in which resonances were observed at low temperatures.

The result for the power absorbed, P, when sweeping through a line is:

$$P=C\left\{\frac{(B^2-A^2)[(1+x^2)^{\frac{1}{2}}+1]^{\frac{1}{2}}}{(1+x^2)^{\frac{1}{2}}}+\frac{2AB[(1+x^2)^{\frac{1}{2}}-1]^{\frac{1}{2}}}{(1+x^2)^{\frac{1}{2}}}(\text{sign of } x)\right\}. \quad (3.9)$$

The experimentally measured quantity is the derivative of the power absorbed with respect to the field:

$$\frac{dP}{dH}=C'\left\{\frac{B^2-A^2}{2}\times\frac{[2+(1+x^2)^{\frac{1}{2}}][(1+x^2)^{\frac{1}{2}}-1]^{\frac{1}{2}}}{(1+x^2)^{\frac{3}{2}}}(\text{sign of } x)+AB\frac{[(1+x^2)^{\frac{1}{2}}-2][(1+x^2)^{\frac{1}{2}}+1]}{(1+x^2)^{\frac{3}{2}}}\right\}, \quad (3.10)$$

where

$$C=\tfrac{1}{4}\omega H_1{}^2(\Lambda A)\omega_0\chi_0(6T_2\tau)^{\frac{1}{2}}(C^2/4\pi\omega\Lambda)^2,$$

$$C'=\gamma T_2 C.$$

A and B are defined by the complex impedance $Z=A+iB$. They are functions of the classical skin depth and the mean free path. Their ratio may be conveniently read off from Reuter and Sondheimer[4] (Fig. 1). For the region of the completely anomalous skin effect, $B/A=\sqrt{3}$. For this case, expressions (3.9) and (3.10) are plotted in Fig. 11. Taking the resistivity data of MacDonald and Mendelssohn[3] for pure sodium at 4°K, one obtains the parameter, α, defined by Reuter and Sondheimer,

$$\alpha=\tfrac{3}{2}(\Lambda/\delta_0)^2\cong 4\times 10^5 \text{ at } 300 \text{ Mc/sec.}$$

This is well in the region of the completely anomalous skin effect.

Figure 12 shows the agreement between the experimental curve and the theoretical expression for sodium at 4°K and 300 Mc/sec.

C. Relaxation Times *vs* Temperature

1. *Experimental Results*

The metals in which resonances were observed may be conveniently divided into two groups, according to the temperature dependence of their relaxation times. In Li and Be, the relaxation time is temperature independent whereas in Na and K it varies with temperature. The signal to noise ratio for the K sample was too poor to get accurate data. Since the line shape in K could not be checked against Dyson's theoretical curves, there exists a slight doubt as to whether the signal was due to conduction electrons. The measurements were made at 300 Mc/sec.

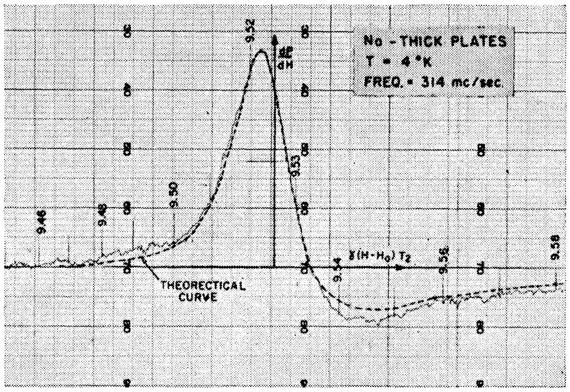

FIG. 12. Comparison between theory and experiment of the electron spin resonance absorption in the region of the completely anomalous skin effect.

Na, K.—The relaxation time *vs* temperature for sodium is plotted in Fig. 13, from which we see that $T_2 \sim 1/T$.

For K we observed only a signal at 4°K which gave an estimated

$$T_2=5\times 10^{-9} \text{ sec.}$$

If the line width had stayed constant on heating up the sample, the amplitude of the observed signal should have increased (because of the increase in skin depth). Since, however, no resonance was observed above 4°K,

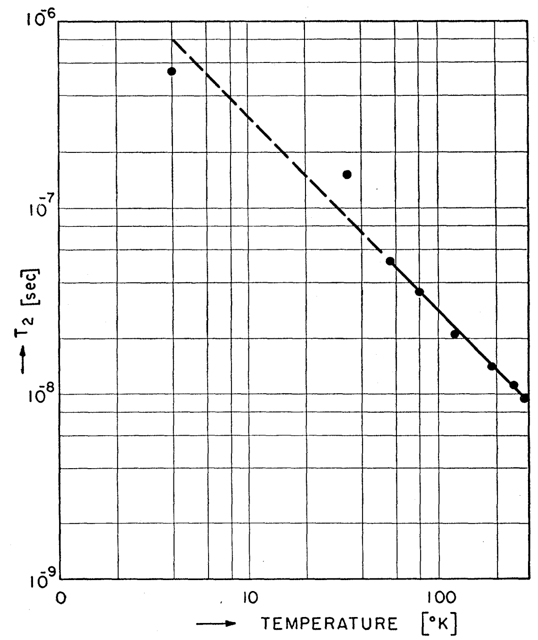

FIG. 13. Electron spin relaxation time T_2 *vs* temperature in sodium.

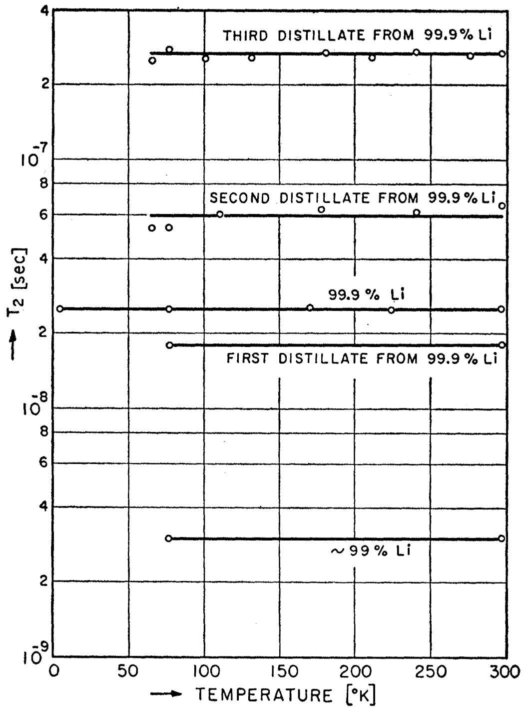

FIG. 14. Electron spin relaxation time T_2 *vs* temperature for lithium samples of different purity.

it must be concluded that the line width increases (T_2 decreases) with temperature.

Li, Be.—The relaxation time in both metals stayed constant in the temperature range between 4°K and 296°K.

From Fig. 14, we see that the relaxation time in lithium increases from 3×10^{-9} to 2.5×10^{-8} sec, upon purification of the sample from 99.0 percent to 99.9 percent. This strongly suggests that the relaxation is associated with impurities, rather than the metal proper. To prove this point even more conclusively, several distillates were taken from the 99.9 percent pure material (for the techniques see Sec. III). The first distillate had a shorter relaxation time ($T_2=1.8\times10^{-8}$ sec) than the subsequent ones ($T_2=6\times10^{-8}$ sec and 2.7×10^{-7} sec respectively). This result, besides proving the point made earlier, shows that the impurities responsible for the relaxation mechanism have a higher vapor pressure than lithium. It would be very desirable to purify the lithium further in order to get the "true" relaxation time.

Several different samples of beryllium were tried, but only one, supplied by the French Company, Pechiney (their U. S. representative is International Selling Corporation, 122 East 42nd Street, New York 17, N. Y.), and quoted to be 99.5 percent pure, gave a resonance signal. The relaxation time was temperature independent and had a value of

$$T_2=2.0\times10^{-8}\text{ sec.}$$

The temperature independence of T_2 suggests again an impurity scattering mechanism. The samples which showed no resonance had presumably a higher impurity concentration. (These were supplied by Brush Beryllium Company, and Fairmont Chemical Company. We are also indebted to Professor E. Segrè for supplying us with beryllium sheets.) This would broaden the line and consequently reduce the signal below the noise level. This could also explain the failure of Gutowsky and Frank[5] to observe a resonance in beryllium.

2. *Comparison of Experimental Results with Overhauser's and Elliott's Theory*

The paramagnetic relaxation in metals was treated by Overhauser.[6] His shortest relaxation time is 8×10^{-7} which is two orders longer than the experimentally observed value in sodium. This particular mechanism has also a field dependence which should increase the relaxation time by 40 percent when going from 300 Mc/sec (~100 oersteds) to 9000 Mc/sec (~3000 oersteds). The experimentally determined ratio of T_2 for these two frequencies for the same sodium sample was found to be (T_2 at 100 oersteds)/(T_2 at 3000 oersteds) $=1.05\pm0.05$. This result indicates that the above relaxation mechanism is not merely off by a proportionality constant.

It is of interest to note that the interaction of the spins with longitudinal phonons gives the observed temperature dependence in Na but is off by 4 orders. The large discrepancy between Overhauser theory and the experimental results is probably due to his assumption of plane waves for the electronic wave functions.

Before leaving his theory, one result is worth noticing. The spin-spin interaction, which would broaden the line without providing a spin lattice relaxation mechanism, is completely negligible. This is the theoretical justification for setting $T_1=T_2$. The experimental proof was given by Slichter[6] who demonstrated the validity of this relation from saturation measurements.

Another possible explanation for the spin relaxation mechanism has been suggested by Elliott,[7] who considered the effect of spin-orbit coupling on the relaxation time. Since the interaction of the lattice with the motion of the electrons is very large in comparison with the direct interaction of the spins with the lattice, a very small coupling of the spins to their orbits will provide a very effective relaxation mechanism. His result for the spin relaxation time T_1 is [see Eq. (59), reference 7]

$$T_1=\alpha[\tau_R/(\Delta g)^2], \tag{3.13}$$

where α = numerical factor smaller than 1; if one assumes the simple Debye theory for the lattice waves, $\alpha\cong1/30$; τ_R = the usual relaxation time obtained from resistivity measurements; $\Delta g=(g-2.0023)$ deviation of

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[5] H. S. Gutowsky and P. J. Frank, Phys. Rev. **94**, 1067 (1954).

[6] A. W. Overhauser, Phys. Rev. **89**, 689 (1953).

[7] R. J. Elliott, Phys. Rev. **96**, 266, 280 (1954).

the electronic g value from the free electron value; this is a measure of the amount of spin-orbit coupling.

For sodium, $\tau_R=3\times10^{-14}$, $\Delta g=8\times10^{-4}$ (see next section), we get for T_1 a value of 2×10^{-9}. Comparing this figure with the experimentally observed value of 9×10^{-9}, we see that there is fair agreement.

This relaxation mechanism predicts that T_1 should be proportional to T for temperatures above the Debye temperature and $1/T^3$ below the Debye temperature. The resistivity varies at $1/T^5$ but the extra factor of $1/T^2$ discriminates against forward collisions, which do not contribute to the resistivity but are equally effective in flipping spins. Sodium has a Debye temperature of 200°K, so that according to Elliott the relaxation time should start to fall off faster than T below this temperature. This is in variance with the experimental results.†

The attractive features of Elliott's mechanism are that it explains the shortening of the relaxation time with increasing spin-orbit coupling, which is in accord with the observed results in the alkali metals. If the spin-orbit coupling is too large, the line would be broadened to such an extent that it would be impossible to observe a resonance. All metals in which we were unsuccessful in observing a resonance had larger spin-orbit couplings than the ones in which a resonance was observed. This mechanism also explains the importance of impurities having a larger spin-orbit coupling than the host metal. The presence of impurities would certainly be most important for Li which has the smallest spin-orbit coupling of all the metals, and thus explains the observed results very well.

D. Electronic *g* Values

All the g determinations were made at 3 cm by comparison with the organic free radical diphenyl picryl hydrazyl.[8] For Li and Na the free radical was introduced into the cavity simultaneously with the bulk metal sample and covered its entire area. This eliminated any errors arising from field inhomogeneities. Since the g values of Be and the free radical lie very close together, the two resonance lines overlapped and alternate runs, with and without the free radical, had to be made. In each case at least 10 runs were made. The experimental results, together with the theoretically calculated values,[9–11] are listed in Table I. For sodium, Brooks' calculations, based essentially on the atomic spin-orbit coupling constants, agree within the experimental error.

Table I. Experimental and theoretical values for the g shift, $\Delta g=(g-2.0023)$.

Metal	Experimental values	Theoretical values
Li	$\Delta g\leq10^{-4}$	-6×10^{-5} (Argyres and Kahn[a])
Na	$\Delta g=-(8\pm2)\times10^{-4}$	-3.7×10^{-4} (Yafet[b]) -6.6×10^{-4} (Brooks[c])
Be	$\Delta g=+(9\pm1)\times10^{-4}$	No theory

[a] See reference 9.
[b] See reference 10.
[c] See reference 11.

Up to the present time there have been no theoretical calculations made on the g shift in beryllium. In beryllium the $2s$ band may be nearly filled, some electrons spilling over into the next zone. The resonance from those electrons would give a negative g shift, while the holes in the $2s$ band would give a positive g shift. If the electronic transitions into the $2s$ band are fast in comparison to a spin relaxation time, we would not expect to see two separate lines, but a single line as observed. The g of this line would fall between the two values. The fact that in Be the g shift is definitely positive suggests that the energy surfaces at the top of the $2s$ band may be degenerate (or nearly so) in which case we would expect a large positive g shift.[7]

The g shift in Li was too small to observe experimentally. The theoretical value is 10 times smaller than that of Na. If one assumes Elliott's relaxation mechanism, this would mean that the relaxation time in pure Li should be 100 times longer than in sodium, i.e., approximately 10^{-6} sec. The experimentally observed value in the purest Li so far obtained is about 4 times shorter than this. An impurity content of only about 1 part in 10^5 of rubidium or cesium, having spin-orbit couplings roughly 1000 time larger than Li, could account for such a shortening of the relaxation time. However, it should be pointed out that a temperature-dependent relaxation time of 10^{-6} sec should already have shown up in the experimental data on the purest Li (see Fig. 14). The failure to observe such a temperature dependent contribution means that the estimated spin-orbit coupling in Li is too large. A further purification of the Li would be very instructive.‡

E. Absolute Values of the Paramagnetic Susceptibility

In our experiments we obtain the paramagnetic contribution to the susceptibility by comparing the integrated resonance absorption in the metal to that of a known amount of the organic free radical diphenyl picryl hydrazyl. The alkali metal sample is in the form of a film, thin in comparison to a skin depth (1–2 microns), which is evaporated on a sheet of mica. (See Sec. III.) The exact amount of metal is obtained by

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† *Note added in proof.*—Y. Yafet (private communication) re-examined Elliotts' mechanism and concluded that T_1 is proportional to $1/T$ also below the Debye temperature. This is essentially due to the overwhelming contribution of low-energy phonons to the relaxation mechanism.

[8] C. A. Hutchison and R. C. Pastor, Phys. Rev. **81**, 1282 (1951).

[9] P. Argyres and A. Kahn (to be published).

[10] Y. Yafet, Phys. Rev. **85**, 478 (1952).

[11] H. Brooks, Phys. Rev. **94**, 1411(A) (1954).

‡ *Note added in proof.*—Recently the g-value of cesium was found to be 1.93±0.02 (G. Feher and R. A. Levy; Berkeley Meeting, December 28, 1954) which compares favorably with Brooks' result of 1.94.

allowing it to react with ethyl alcohol and measuring the amount of hydrogen evolved. However, this work is only in its early beginnings and at present our experimental error exceeds that of other workers.[12] More work is being done at present to improve this method.

In principle one could use the results on thick plates to determine the susceptibility with the aid of Eq. (3.3). However, in this case, surface irregularities and the lack of knowledge of the resistivity of the material will severely limit the accuracy with which the susceptibility can be determined. In spite of this inaccuracy we used beryllium particles (not having thin films available) large in comparison to a skin depth in order to get at least a rough estimate for the susceptibility. The value obtained was $\chi_0 \cong 2\times 10^{-7}$ cgs volume units. In this case there entered an additional error due to the fact that the exact particle-size distribution was not known. The only justification to quote such a rough estimate is that to our knowledge there is no other published experimental value for the paramagnetic susceptibility of beryllium.

F. Metals in which no Resonance was Observed

Aluminum and magnesium was investigated at 300 Mc/sec in the temperature range between 4°K and 300°K, palladium and tungsten between 77°K and 300°K. In none of the metals a resonance was observed. From the knowledge of the sensitivity of the equipment, this result establishes an upper limit to the spin relaxation time at room temperature of the above metals of $T_2 < 5\times 10^{-10}$ sec. It is difficult to estimate an upper limit of T_2 at 4°K, since the residual resistance, which strongly affects the diffusion time and hence the expected signal, was not known.

The short relaxation times can be explained easily if we assume Elliott's relaxation mechanism.[7] The spin-orbit couplings in the above metals are at least an order larger than in sodium, which would make the relaxation time approximately 2 orders shorter, i.e., 5×10^{-11} sec. The Russian workers, Al'tshuler, Kurenev, and Salikhov[13] report for tungsten a line width of 40 oersteds ($T_2 \approx 10^{-9}$ sec) at 240 Mc/sec. In a later article Salikhov's[14] value for tungsten is approximately 1000 oersteds ($T_1 \approx 5\times 10^{-11}$ sec). (No explanation or mention of the earlier value is made.) In his article resonances in 19 metals are reported, all of them having roughly the same line width (500–1000 oersteds). Comparing their results with ours on the alkali metals, there exists an alarming discrepancy. Their line width in lithium is roughly 3 orders broader than ours. Their g value for lithium is 2.92, which makes their g shift at least 2–3 orders longer than ours. Their curve for aluminum shows no trace of a "Dysonian character," which makes it questionable whether they observe resonances due to conduction electrons. It should be mentioned that in our early experiments large resonance signals were observed in aluminum. However, they were traced to ferromagnetic impurities (at the low fields used there is an appreciable hysteresis associated with the signal), and they disappeared when high purity materials were used. Also, care has to be taken in the choice of sample holder. Both glass and polystyrene give resonances at $g=4$ and $g=2$. The signal from the latter is very weak and was only observed at 4°K when an excessive quantity of it was used.

APPENDIX A. JUSTIFICATION FOR NEGLECTING SURFACE RELAXATIONS IN THICK PLATES

Dyson finds for the total spin relaxation time T_2 in particles small in comparison to a skin depth (D-105):

$$1/T_2 = 1/T_1 + 1/T_S, \tag{A.1}$$

where T_1 is the usual spin-lattice relaxation time and T_S for small particles is given by (D-108):

$$T_S = (4/3)(r/\epsilon v), \tag{A.2}$$

where r = radius of particles, ϵ = probability of a spin disorientation during a surface collision, and v = velocity of electrons at the top of the Fermi surface. For our case (see Sec. IV),

$$T_S = 2\times 10^{-8}\ \text{sec}, \quad r \cong 2\times 10^{-4}\ \text{cm}, \quad v = 10^8\ \text{cm sec}^{-1},$$

which gives a value for $\epsilon \cong 10^{-4}$.

The important parameter describing the effect of surface relaxations on the line shape is ψ. (D-110)

$$\psi = \epsilon\left[\tfrac{3}{8} T_2/\tau\right]^{\frac{1}{2}}, \tag{A.3}$$

where τ = relaxation time obtained from resistivity measurements. For ψ small in comparison to 1, the change in line shape due to surface relaxations may be neglected. Substituting the experimental values into (A.3) we get $\psi = 0.03$.

ACKNOWLEDGMENTS

We would like to express our thanks to Professor C. Kittel, for several helpful suggestions. We gratefully acknowledge the cooperation of the Aluminum Corporation of America and the Dow Chemical Company, who prepared for us the high-purity aluminum and magnesium foils. We wish to thank M. Browne for his general assistance, especially the evaporation work; Dr. J. Ubbink for his assistance on many low-temperature runs; also Dr. T. W. Griswold who collaborated in the early experiments; and M. Levy who computed most of the Dyson curves. This work was assisted in part by the Office of Naval Research and the U. S. Signal Corps.

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[12] Schumacher, Carver, and Slichter, Phys. Rev. **95**, 1089 (1954).

[13] Al'tshuler, Kurenev, and Salikhov, Doklady Akad. Nauk. S.S.S.R. **84**, 677 (1952).

[14] S. G. Salikhov, Akad. Nauk. S.S.S.R. **16**, No. 6, 748 (1952).

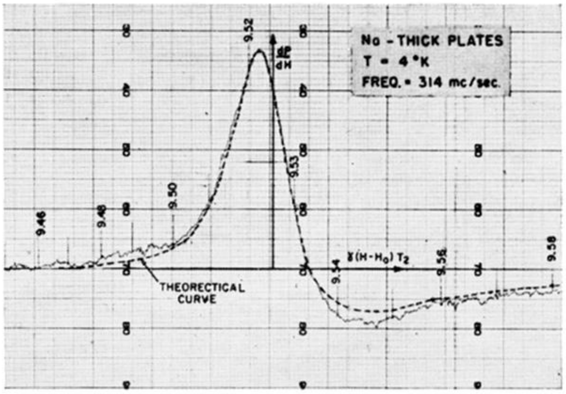


FIG. 12. Comparison between theory and experiment of the electron spin resonance absorption in the region of the completely anomalous skin effect.

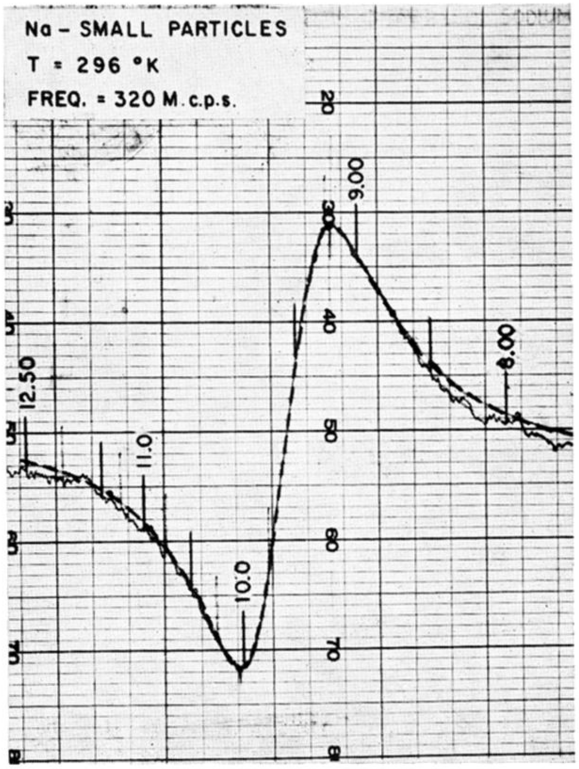
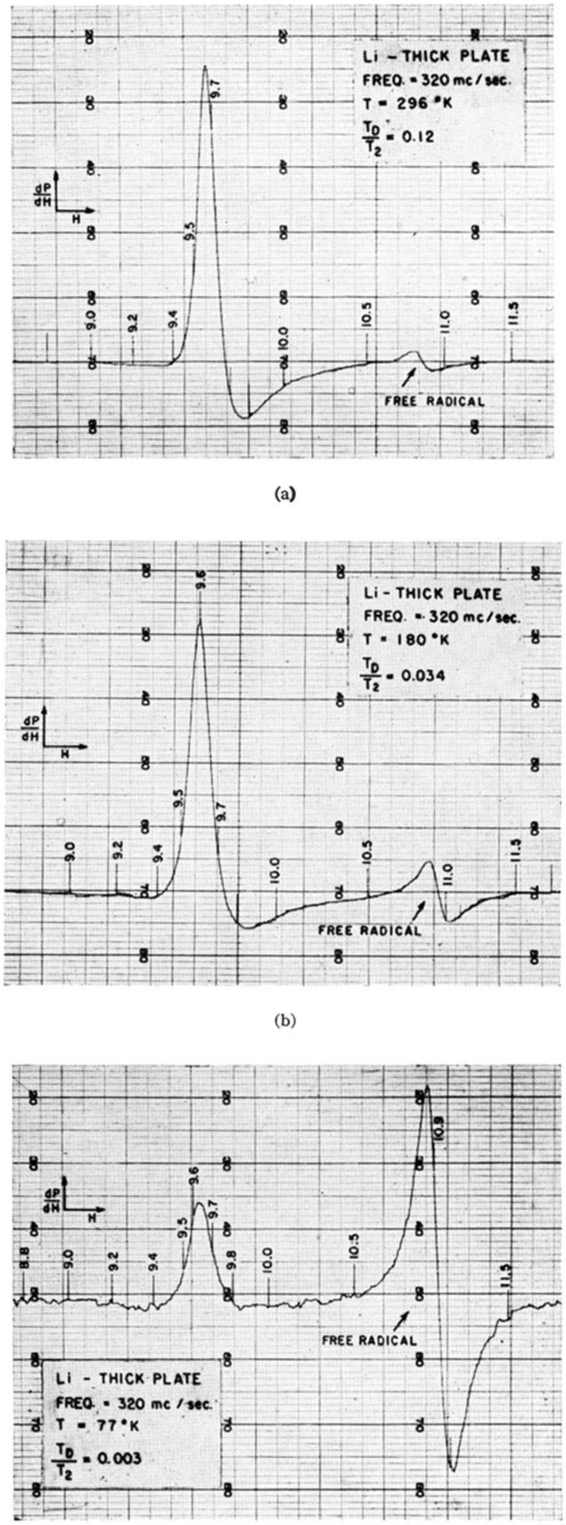


FIG. 8. Electron spin resonance absorption in small sodium particles. Diameter of particles smaller than 5 microns.



(a)

(b)

(c)

FIG. 9 (a, b, c). Electron spin resonance in thick plates of lithium for different ratios of T_D/T_2. Markers are proportional to the magnetic field. 1 unit = 11.77 oersteds. Compare the shape with the theoretical curves of Fig. 3.