Dynamic Nuclear Enhancement in Metallic Sodium*

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(Received 27 August 1964)

A double-resonance spectrometer was constructed capable of making accurate measurements of all the dynamical variables expressed in the master equation governing the time evolution of the dynamic nuclear enhancement of a single sodium sample. This system could measure the rate of rise of the nuclear polarization after the onset of saturation, the rate of decay of the polarization after the saturation was removed, and the nuclear T_1 by the standard 180°-90° pulse method. It was found that each of these processes had the same time constant $T_1=13.2\pm0.2$ msec within experimental error, in agreement with theory. The steady-state enhancement as a function of electron saturation gave a value of the "leakage coefficient" f to be 0.88 ± 0.05 (at 29°C). The values of T_1 and f enable one to calculate T_1^e (the spin-lattice relaxation time due to the conduction-electron-nuclear contact interaction) to be 14.9 ± 0.8 msec. These data demonstrate that the electron-nuclear contact interaction is the dominant mode of nuclear relaxation for sodium at room temperature.

I. INTRODUCTION

IN 1953, Overhauser[1] predicted that the saturation of the conduction-electron spin resonance in a metal would produce a large increase in the nuclear polarization for metals whose nuclei approach thermal equilibrium with their lattice predominantly by means of the magnetic Fermi hyperfine interaction with the conduction electrons. Since this first theoretical paper, many authors[2] have demonstrated both experimentally and theoretically the existence of this and similar effects in a variety of substances and with a variety of "pumping" procedures. In the first experimental verification of the existence of the Overhauser effect, Carver and Slichter[3] measured the dynamic enhancement of sodium, lithium, and sodium-ammonia solutions. Although these experiments clearly demonstrated the existence of the effect, the data did not permit a good quantitative check on all the dynamical variables involved in this polarization technique. These early measurements on sodium did seem to indicate, however, a significant discrepancy with Overhauser's theory. This was a surprising result since the electron-nuclear coupling in sodium had been studied thoroughly by pulsed nuclear-resonance techniques[4] and by cw techniques at low temperature.[5] The results of Carver and Slichter seemed to indicate that at room temperature the Fermi contact interaction accounted for only about half the nuclear spin-lattice relaxation mechanism while the other experimental data showed that this coupling would account for all of the relaxation process.

In order to eliminate most of the ambiguities in the early experiments and to verify the theory of Overhauser's, a double-resonance spectrometer was constructed which was capable of measuring directly and accurately all the observable dynamical variables expressed in the master equation governing the time evolution of this type of dynamic nuclear enhancement on a single sample.[6] In this way we hoped to be able to demonstrate the quantitative validity of the theory. Independent experiments by Hecht and Redfield[7] have also conclusively confirmed the theory of Overhauser for sodium and lithium in the low-temperature case. In Sec. II a brief presentation of the theoretical master equation is given along with its solution as applied to the various experiments performed. Section III is a discussion of the design of the apparatus. Section IV deals with the specific data obtained for sodium.

II. MASTER EQUATION

A complete theoretical treatment of dynamic enhancement in solids has been worked out by Abragam.[8] The master equation derived for the time evolution of the expectation value of the z component of the nuclear magnetization $\langle I_z\rangle$ is

$$\frac{d\langle I_z\rangle}{dt}=-\left(\frac{1}{T_1}\right)\left\{\langle I_z\rangle-I_0\left(1-f\frac{\gamma_e}{\gamma_n}\left[\frac{\langle S_z\rangle-S_0}{S_0}\right]\right)\right\}, \quad (1)$$

where T_1 is the total nuclear spin-lattice relaxation time, γ_e and γ_n are the electronic and nuclear gyromagnetic ratios, respectively, I_0 the thermal equilibrium nuclear magnetization, $\langle S_z\rangle$ the expectation value of the z component of the electronic magnetization, and S_0 the thermal equilibrium electronic magnetization. The "leakage coefficient" f is defined in Eq. (2) as

$$f\equiv\frac{(1/T_1^e)}{(1/T_1)}, \quad (2)$$

* Supported by the U. S. Air Force Office of Scientific Research, U. S. Air Force.

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[1] A. W. Overhauser, Phys. Rev. **91**, 476 (1953); **92**, 411 (1953).

[2] For a nearly complete bibliography of the work on this subject see Robert Webb, Am. J. Phys. **29**, 428 (1961).

[3] T. R. Carver and C. P. Slichter, Phys. Rev. **102**, 975 (1956).

[4] D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1953).

[5] A. Anderson and A. G. Redfield, Proceedings of the International Conference on Low Temperature Physics, Madison, Wisconsin, August 1957 (unpublished).

[6] J. F. Reichert and J. Townsend, Bull. Am. Phys. Soc. **8**, 35 (1963).

[7] R. Hecht and A. G. Redfield, Phys. Rev. **132**, 972 (1963).

[8] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. IX.

where T_1^e is the nuclear spin-lattice relaxation time due *only* to the Fermi hyperfine contact interaction between the electrons and nuclei. Since the total nuclear relaxation time due to all spin relaxation processes may be written as

$$1/T_1=1/T_1^e+1/T_1', \tag{3}$$

where T_1' is defined as the relaxation time due to mechanisms as yet unspecified, we see that a measurement by dynamic polarization of both f and T_1 would permit the calculation from (2) of T_1^e and T_1'. Both the absolute value and the temperature dependence of T_1^e have been the subject of extensive theoretical study.[9]

The transient solutions to Eq. (1) are obvious from inspection if it is assumed that $\langle S_z\rangle$ is time-independent for constant saturating fields. This is an excellent assumption for the experiments performed on the alkali metals, since in this temperature range the electron spin-lattice relaxation time is of the order of 10^{-8} sec while the nuclear relaxation times are about 10^{-2} sec.[10] That is, upon application of the electron saturating field the electronic spin system reaches steady state in a time very short compared to the time necessary for any change to take place in the nuclear spin system. In the experiments described, the time courses of the following processes were measured: (1) the rise of the nuclear polarization after the onset of electronic saturation, (2) the decay of the polarization after the removal of the electron saturation, (3) the return of the unenhanced nuclear polarization to its thermal equilibrium value after a 180° pulse on the nuclear spins. The transient solution to the master equation (1) shows that the nuclear polarization has an exponential time dependence with a single time constant T_1 for all three cases.

The steady-state solution to Eq. (1) (where $d\langle I_z\rangle/dt=0$) can be written immediately as

$$A-1=\left[\frac{S_0-\langle S_z\rangle}{S_0}\right]f\left|\frac{\gamma_e}{\gamma_n}\right|, \tag{4}$$

where the "enhancement" A is defined as the ratio of the enhanced to the unenhanced nuclear polarization $\langle I_z\rangle/I_0$. The quantity in the square brackets is called the saturation parameter s. Since the electron-spin resonance for the alkali metals obeys the Bloch equation with $\tau_1=\tau_e$ (electron-spin relaxation times), it can be easily shown that the saturation parameter can be written as

$$s=\gamma_e^2H_1^2\tau_1^2/(1+\gamma_e^2H_1^2\tau_1^2), \tag{5}$$

where H_1 is the rotating uhf field at the sample. Thus, Eq. (4) can be written in terms of experimentally measurable quantities (the sodium electron linewidth ΔH_{Na}; half-width between points of maximum slope) as

$$A-1=\left[\frac{H_1^2}{3(\Delta H_{\mathrm{Na}})^2-H_1^2}\right]\frac{\gamma_e}{\gamma_n}f \tag{6}$$

with f as the only unknown. The technique for measuring f will be described later.

III. APPARATUS AND EXPERIMENTAL CONSIDERATIONS

The dc magnetic field will uniquely determine the electronic and the nuclear Larmor frequencies in a double-resonance experiment. Considering only detection of the nuclear resonance signal, it is well known that the signal-to-noise ratio improves with increasing magnetic field. Since the enhancement parameter A is the ratio of the enhanced to the unenhanced signal, the accuracy with which one can measure it, and consequently calculate f from Eq. (6), will largely depend upon the errors inherent in the measurement of the unenhanced signal I_0. Thus from this consideration alone, it is apparent that the largest H_0 field possible is desirable. However, from the point of view of the experimental feasibility of electronic spin saturation, a low H_0 field is indicated for three reasons:

(1) Skin Depth

It is well known that radio-frequency waves are attenuated as they penetrate electrically conducting media. Since it is necessary for accurate measurements of the Overhauser enhancement to have uniform saturating rf fields throughout the sample, it is necessary to divide the sample into particles having a size of the order of the skin depth or less at the frequency used. Because the skin depth varies inversely with the square root of the frequency, the problem of uniform saturation is reduced by decreasing the electron saturating frequency and hence H_0.

(2) Electron Saturating Power

In order to obtain appreciable enhancement of the nuclear polarization, it is necessary to achieve a reasonable degree of electronic saturation. To achieve such a saturation for sodium, whose electron linewidth is rather broad (4.5 G), power levels on the order of hundreds of watts are necessary. Such power levels are progressively harder to achieve at the higher frequencies.

(3) Induction Heating

Magnetic induction heating of small metallic particles can also become a serious problem for the large oscillating magnetic fields needed to saturate these electron-spin resonances. A simple calculation based on the assumption that the field penetration is uniform shows that, for a fixed H_1 amplitude, power dissipated in a spherical particle per unit volume is proportional to

[9] J. Korringa, Physica **16**, 601 (1950).
[10] G. Feher and A. P. Kip, Phys. Rev. **98**, 337 (1955).

the frequency squared and particle radius squared. At sufficiently high frequencies this "flash" heating, during electron-saturating pulses, can become a difficult problem since the dynamic polarization is temperature-dependent.

Sample Preparation

We were able to divide the alkali metal into particles 3-4 μ in diameter by means of ultrasonic agitation at 500 kc/sec with a 900-W generator. Alkali metal pieces were placed with Ceresin wax in a nickel container having a thin tantalum foil (0.001-in.) bottom acting as an ultrasonic window. The container was placed in an oil bath which served as a transmission medium for the ultrasonic power from the transducer to the window. The wax and the alkali metal were heated to the melting point of the metal during the ultrasonic agitation. The samples were made by dispersing them for about four hours at full ultrasonic power. The remaining large particles were sedimented out by placing the sample in a column for about an hour. Microscopic examination of the remaining sample showed that the sample consisted of particles whose diameter ranged from 1 to 5 μ with the peak of the distribution at about 3 μ.

To check the feasibility of uniform electron saturation at x-band frequencies, an electron-spin resonance was run on the sample at this frequency. Dyson[11] has shown that an asymmetry in the line shape of the electron-spin resonance of a metal indicate a nonuniform penetration of the oscillating magnetic field throughout the sample. The measurement of this asymmetry was the criterion used in this experiment to determine the uniform penetration of the saturating microwave field. At x band some asymmetry was observed, but at 1000 megacycles no asymmetry could be observed. From this consideration, 1000 megacycles was chosen as the frequency to use in the experiment.

In order to obtain an appreciable unenhanced nuclear-resonance signal, the dispersed particles were concentrated by sedimentation for 30 h into the glass sample holders. The glass tubes were then sealed to prevent oxidation. The heat created by the large uhf saturating fields was removed by surrounding the sample with a rapidly flowing air stream and by flowing air down a small glass tube running coaxially through the center of the sample holder. This reduced the temperature differences throughout the sample to less than 1°C for the largest saturating fields.

Cavity Design

A straightforward calculation of the oscillating magnetic field in a simple rectangular cavity operated in the TE_{102} mode at 1000 megacycles shows that it requires some 10^4 W to produce a rotating field of 8 G if the cavity has a loaded Q of about 500. Such power levels become prohibitively expensive at 1000 megacycles. The large power is required essentially because of the large volume of space in which one is storing the electrical energy in this cavity. It is possible to reduce this volume drastically by use of line resonators. The line resonator designed for this experiment is shown in Fig. 1.

The electric field of this resonator is concentrated in its wings, while the magnetic field is nearly uniform down the center axis. There are two physical pictures one can use to understand this resonator. One may consider the low-frequency analog: a series tuned circuit has two coupled inductors (formed by the large square cross section) and two tuning capacitors (the flat wings). The magnetic field strength along the symmetry axis closely resembles that of a long solenoid, so this is a useful analog. However, since the wavelength of its resonant frequency is comparable to its physical dimensions, the low-frequency analog is suspect. One may wish to consider the field approach by recalling the standing-wave pattern for a parallel-plate transmission line one-half wavelength long. If we now compress the electric field into a small region by narrowing the spacing near the ends (the electric-field maxima), we have essentially the resonator shown. It need only be shown that such a device can set up standing waves internally. The experimental fact that such a device, properly shielded from radiation losses, does resonate with unloaded Q of about 2000 demonstrates this clearly.

Since this resonator has an effective volume some two orders of magnitude smaller than the TE_{102} rectangular cavity (60 cm^3 versus 6000 cm^3) the input power is proportionately less by two orders of magnitude. High-power air-cooled tetrodes designed for uhf television service were used to furnish the saturating power for the resonator.

Compatible NMR System

Having made the choice of frequencies and designed a high-filling factor line resonator whose oscillating magnetic field is uniform over approximately 6 cm^3, the next step was to design a sensitive low-frequency nuclear resonance spectrometer which was compatible with the uhf system. One of the serious problems in many of the previous experiments on the Overhauser effect was the unknown shielding of the saturating field by the nuclear receiver coil. Because the unenhanced nuclear-resonance signal is extremely small it is imperative to have a nuclear receiver coil with a high-filling factor. This meant that a receiver coil had to be designed which could be placed round the sample holder and inside the line resonator, but would not obstruct the mircowave field. Early attempts at using ordinary cylindrical-coil geometries but with spaced windings of fine wire were unsuccessful. The coil shown in Fig. 1, wound close-spaced, seemed to have little perturbing effect on the microwave field configuration. The principal axis of this coil is in the horizontal plane, while

[11] F. Dyson, Phys. Rev. **98**, 349 (1955).

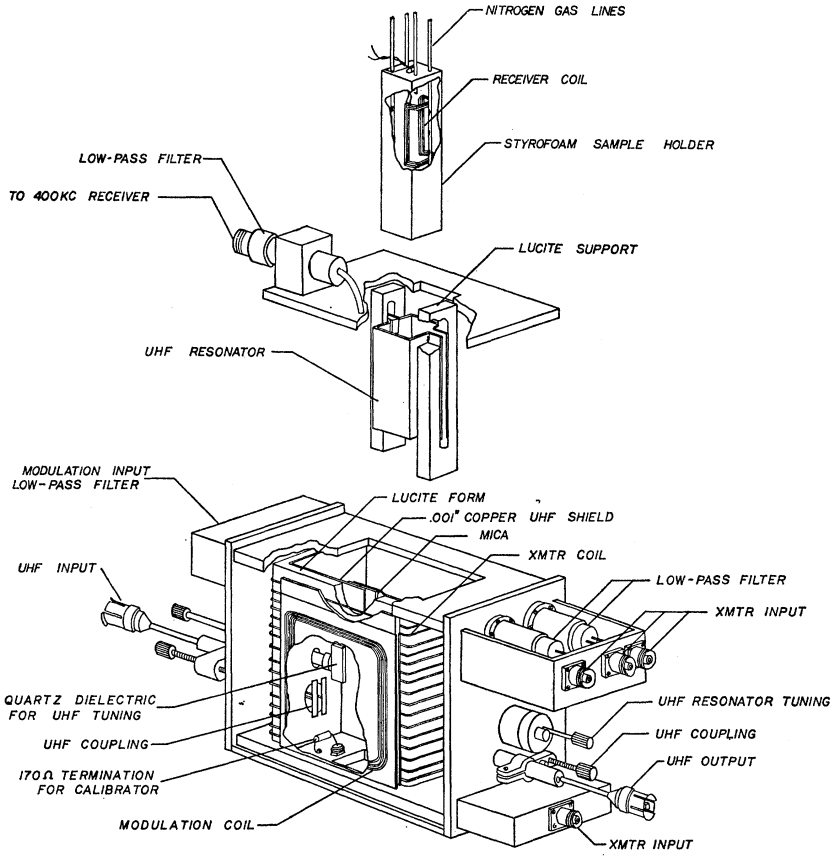

FIG. 1. Exploded view of double-resonance system. Line-resonator dimensions are $3\frac{1}{4}$ in. long with a $1\frac{1}{16}$-in. square cross section and capacitance wings $\frac{5}{8}$ in. extended from the main body.

the microwave field is free to propagate along the vertical axis because of the peculiarly designed ends. The Q of the uhf resonator is reduced by the presence of this receiver coil, but because of the lossy metallic sample, this effect is largely masked. Because it was necessary to wind this receiver coil with such a geometry and because of the proximity of the resonator's conducting walls, the coil's Q was limited to about 50. This and the volume of the sample limited the nuclear resonance signal-to-noise ratio.

With the 1000-megacycle line resonator and a compatible 400-kc/sec receiver coil, the design of the remainder of the components was relatively straightforward. The line resonator, supported by two Lucite posts, is placed in the center of the brass box. To prevent this resonator from radiating its energy into space, a cylindrical shield of 0.001-in. copper is placed around it on the inside of a plastic form. This is not a continuous piece of copper but is joined by forming a uhf capacitor out of 0.001-in. mica and the overlapping ends of the sheet. This provides a good uhf short but does not act as a short circuit for the low-frequency transmitter tank coil wrapped on the outside of this form. The line resonator is tuned by two quartz slabs which can be inserted on both sides of the resonator in the high-electric-field region. To maintain a good electric-field node at the sample in the center plane of the resonator, it was necessary to tune both slabs simultaneously.

Microwave coupling to the line resonator is provided by electric field excitation. This proved to be more convenient than magnetic field coupling, since it left the ends of the resonator unobstructed. Two baluns transformers allowing transitions from balanced to unbalanced transmission line with plates attached to the ends of their balanced lines, provide a symmetric electric field for the excitation. The coupling is varied by moving the transformers in and out, thus changing the capacitance between the resonator and the plates. The high-power input coupling to the resonator was always adjusted for match, that is, no reflected power from the resonator. The reference detector is fed by the second transformer which is weakly coupled to the resonator.

The transmitter coil for the pulsed nuclear-resonance spectrometer is wound in the form of a long solenoid using the plastic form as a support. Because of the dimensions of this coil, the rf homogeniety of the transmitter field was quite good. This coil form may be easily removed from the box and replaced by removing the Lucite cover plate.

Low-frequency (90-cycle) magnetic-field modulation,

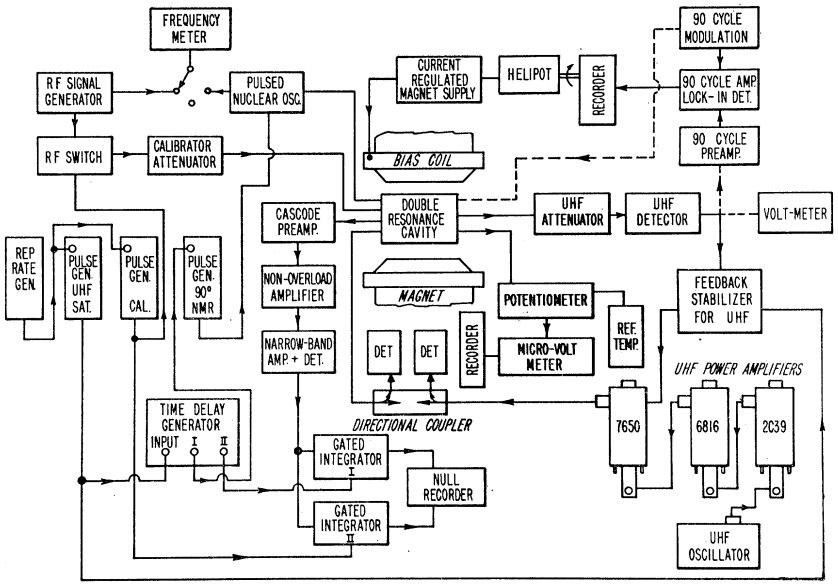

FIG. 2. Block diagram of experimental arrangement of components used in measuring rise time of nuclear polarization after onset of saturation. Modifications of pulse sequences for other experiments are obvious.

parallel to the static field H_0, is provided by a pair of coils mounted on the sides of the box. These coils provide the time-varying magnetic field necessary for the electron spin-resonance spectrometer.

There are four low-pass filters mounted on the box to prevent uhf leakage. Such leakage can lead to detuning and loading of the cavity which are undesirable. In the most critical places, on the oscillator coil and on the receiver coil, folded coaxial line, tuned low-pass filters were used.

A block diagram of all the electronic circuits associated with this double resonance cavity is shown in Fig. 2. This is a complete incoherent pulsed nuclear-resonance spectrometer with a compatible high-power saturating electron-spin-resonance spectrometer. All nuclear polarizations were measured by the initial amplitude of the Bloch decay following a 90° pulse on the nuclear spins. All timing pulses in the various experiments were generated by a set of pulse generators (Textronix 160 series). All the time measurements were made with the accurately calibrated (1%) time delay generator (General Radio model 1392-A). The sample temperature was measured by a fine wire thermocouple embedded in the sample and brought out of the cavity through a simple capacitive uhf bypass filter.

The electron resonance was saturated by a high-power burst from the uhf oscillator and three-stage amplifier shown. The amplitude of the uhf field in the line resonator was stabilized during the pulse by a feedback system to the grid of the final-power amplifier, with the oscillator and two drive amplifiers (6816 and 2C39) run cw. Since the oscillating magnetic field inside the resonator is proportional to the oscillating electric field at the capacitive pickup and this is proportional to the output amplitude from this coupling into a matched 50-Ω load, it was possible to obtain an error signal for the feedback stabilizer by detecting this power using a matched diode detector (Sierra model 148). The difference between the signal and an internally generated reference pulse in the self-stabilizer is amplified by a broad-band chopper-stabilized dc amplifier (Philbrick USA-3) and fed into the control grid of the 7650, completing the feedback loop. As long as the pickup probe and the line resonator remained in the same physical position, the feedback system would keep the pulsed saturating field in the cavity constant even if the resonator or the power amplifiers became untuned, or if the dc input power to the power amplifier was changed. Checks were made on the ability of this system to maintain the pulsed fields in the resonator constant by observing the enhanced Bloch decay while detuning the resonator, changing plate and screen voltages on the power amplifier, and varying the room temperature. For variations ten times those one should reasonably expect to encounter in an experimental run, no observable change could be detected in the enhanced Bloch decay amplitude.

With this stabilization scheme it is quite convenient to change the power delivered to the resonator and hence the square of the saturating field, in precision steps. Placement of various calibrated attenuators between the pickup probe and the detector will, through the self-stabilizer, cause the field in the resonator to be changed in proportional steps. The accuracy of the relative values of the square of the saturating field is limited then by only the precision of the attenuators. The attenuators used in these experiments were calibrated to an accuracy of 3%.

The nuclear pulsed oscillator was a plate-tuned class-C incoherent oscillator with feedback provided by a secondary winding on the tank coil. Extreme simplicity of design for the oscillator was achieved by using

the tank coil as the transmitter coil, thus eliminating all coupling transformers. The nuclear receiver consisted of three parts: a standard broadband cascode preamplifier using a 6BQ7A dual triode, a nonoverload broadband amplifier consisting of a set of three cathode-coupled-clippers in cascade (Cosmic Radiation Labs model 101), and a narrow band (bandwidth of 1300 cycles) tuned amplifier.

The relative amplitude of the Bloch decay for the enhanced and unenhanced signals were measured by a null detection system employing two gated integrators.[12] The essential feature of this method is the use of a calibrated rf signal generator, tuned to the same frequency as Bloch decay, which is introduced as a comparison signal at the receiver coil at a time when the Bloch decay has reached a negligibly small value. One of the gated integrators is triggered to accept a portion of the nuclear-resonance signal, and the other integrator accepts a portion of the comparison signal. The difference in the two signals, averaged over many repetitions of the same experiment, is fed into a null recorder. Thus when the null is achieved, the attenuator gives directly the relative amplitude of the Bloch decay. This system eliminates most of the major stability problems encountered in long runs, such as amplifier center frequency or gain drift, detector calibration in the presence of large noise amplitudes, and detector drifts. The accuracy of this detection system is mainly determined by the rf attenuator used. A Textronix model B170A, 170-Ω attenuator with an accuracy of 1% was used.

IV. DATA

Measurements were made on the relaxation behavior of the nuclear spin system approaching either enhanced steady-state or thermal equilibrium in three different cases. First, the rise of the nuclear polarization after the onset of electronic saturation was measured by sampling the nuclear polarization at measured time intervals following the start of saturation The rise was found to be exponential with a time constant of:

T_1 (growth of polarization) $=13.0\pm0.4$ msec. Second, measurements of the decay rate of the nuclear polarization back to its unenhanced value after the electronic saturation had been removed also were found to give an exponential with a measured time constant of:

T_1 (decay of polarization) $=13.2\pm0.2$ msec. The third case used the standard 180°–90° pulse sequence on the unenhanced nuclear polarization and it yielded:

T_1 (180–90° pulse, unenhanced) $=13.5\pm0.6$ msec. All the above measurements were made at 29°C. The above data clearly show that there is only one relaxation time involved in this dynamic enhancement in agreement with the theory.

The second type of measurement made was on the steady-state enhancement as a function of the electron spin saturation. Equation (6) is the theoretical expression for this measurement. The determination of the enhancement A is straightforward. It is the ratio of the initial amplitude of the Bloch decay immediately following an electron saturating pulse (duration$=10T_1$) to the initial amplitude of the Bloch decay in the absence of electron saturation.

TABLE I. Experimental data.

Attenuation (dB)	H_1^2 (gauss)^2	Saturation parameter "s"	Enhancement "A"	Leakage coefficient "f"
3.03	0.55	0.00885±0.0005	$21.6^{+1.0}_{-0.90}$	$0.945^{+0.095}_{-0.100}$
6.23	1.14	0.0182 ±0.006	$41.2^{+2.0}_{-2.7}$	$0.890^{+0.076}_{-0.085}$
9.43	2.37	0.0369 ±0.0011	$78.5^{+3.8}_{-5.1}$	$0.847^{+0.069}_{-0.079}$
10.13	2.80	0.0433 ±0.0013	$91.2^{+3.3}_{-5.0}$	$0.838^{+0.061}_{-0.070}$

The measurement of the 1000-megacycle saturating field H_1 presents the greatest experimental difficulty. The technique used in this experiment was to measure the line broadening of the electron resonance of DPPH[13] as a function of detected power from the pickup coupler. By placing a jacket of the DPPH around the sodium sample and having both the sodium and the DPPH in the line resonator in close proximity, it was possible to measure the saturation of the electron resonance of the DPPH and calculate the fields at the sodium from these measurements. The equipment modified so as to constitute a standard electron-spin-resonance spectrometer using 90-cycle field modulation was used to measure the linewidth. The magnetic field sweep was accurately measured (1%) by using an incremental gaussmeter (Bell model 240) whose output was fed into the x axis of an x-y recorder (Mosely model 2D). The y axis was taken directly from the output of the 90-cycle phase-sensitive detector. The H_1 field was varied by placing different calibrated attenuators between the pickup coupling and the detector. The electron magnetic resonance linewidth of the DPPH was measured for each value of attenuation and the corresponding H_1 field was calculated. It is well known that the power detected is proportional to the saturating field squared (H_1^2). The data as given in Table I for the four measured points show the above features. This gives an independent check on the H_1 measurements and gives one confidence in their validity.

These data seem to show a systematic decrease in the mean value of the leakage coefficient f with increasing saturating field H_1 although all the values of f over-

[12] A discussion of this technique is fully explained in an article by the authors in Rev. Sci. Instr. **35**, 1692 (1964).

[13] DPPH (Diphenylpicrylhydrazyl) has an extremely large electron spin resonance signal and a narrow linewidth of ½ G. DPPH distilled from benzene (the type used) is known to obey the Bloch equations at room temperature. G. E. Pake (private communication).

lap within experimental error. It is possible that such an apparent decrease in f could be due to flash heating of the metal particles during saturation. Such heating would give rise to a broadening of the electronic linewidth and thus an incorrect value for the saturation parameter s. No estimation of this effect was made in analyzing these data.

The sodium electron linewidth (ΔH_{Na}) given in Eq. (6) was measured with the same electron resonance spectrometer at low rf levels without the DPPH jacket. The measured value at 29°C was $\Delta H_{\mathrm{Na}}=4.54\pm0.07$ G. Thus with the four determinations of H_1 field for the four values of attenuation in the feedback loop of the self-stabilizer and four measurements of the enhancement A for the corresponding H_1 fields, we have made four determinations of the leakage coefficient f. The results are given in Table I. The final value of f taken from these data are

$$f=0.88\pm0.05 \text{ at } 29°\text{C}.$$

The measurement of T_1 and the leakage coefficient f allows us to calculate via Eq. (2), T_1^e, the spin-lattice relaxation time of the sodium nuclei due to their interaction with the conduction electrons only. This value is

$$T_1^e=14.9\pm0.8 \text{ msec at } 29°\text{C}.$$

This quantity has been measured extensively by other techniques[4,5] since it was first predicted theoretically by Korringa. Korringa[9] showed that T_1^e could be related to the Knight shift of the metallic nuclei and was inversely proportional to the temperature. It is because of the latter conclusion that most of the data on nuclear relaxation in metals are quoted in terms of the product $T_1^e\cdot T$, where T is the absolute temperature. For our measurements,

$$T_1^e\cdot T=4.5\pm0.2 \text{ sec-deg}.$$

Redfield[5] measured T_1^eT at low temperatures by assuming that the electron nuclear hyperfine coupling was the dominant mode of relaxation (since relaxation by spin-spin interaction modulated by translation motion and quadrupole relaxation are ineffective). His measurements at 1000 G gave $T_1^e\cdot T=5.1\pm0.3$ sec-deg. Norberg and Holcomb measured this product also and found two values:

$$T_1^e\cdot T=4.77 \text{ sec-deg (at 7950 G)},$$
$$T_1^e\cdot T=4.38 \text{ sec-deg (at 2700 G)}.$$

Our data seem to fall somewhere near the mean of these values. However if the field (or frequency) dependence that Norberg and Holcomb had measured was real, one should have expected our measurements to yield a T_1^eT product lower than 4.38 sec-deg, since the fields we used were only 360 G. An attempt to observe such a field dependence was made with our sample by measuring T_1 at 14 000 G.[14] The value measured was 12.1 ±0.7 msec which is in fair agreement with our 13.1 ± 0.2 msec figure. What is significant however, is that within a field change of a factor of 50 there seems to be only a small change in T_1 in the opposite direction to that observed by Holcomb and Norberg. We feel these experiments indicate that the reported field dependence was spurious.

The measurement of 0.88 for the leakage coefficient shows clearly that the nuclear spin-lattice relaxation is predominantly governed by the electron-nuclear hyperfine coupling. This is what is expected. The earlier results of Carver and Slichter giving a leakage coefficient of 0.5 must now be considered to be incorrect. There are several possible sources for the extra relaxation mechanism (T_1') which give rise to the reduced polarization. The nuclear dipole-electronic dipole interaction with the p character of the conduction band electrons and the interaction of the nuclear dipole-electron orbital motion are unlikely sources since Redfield[7] demonstrated 100% polarization for sodium at helium temperature. The most probable source is the quadrupole relaxation at defect sites in the lattice and nuclear dipole-dipole relaxation. Both these processes would not be operative at low temperatures. Since no temperature-dependent data were taken, and since this relaxation mechanism is extremely small ($T'\sim100$ msec), no conclusive statement can be made as to its precise origin. However, since the value of $T_1^e\cdot T$ presented here also agrees well with other theoretical and experimental evidence, the Overhauser effect in sodium can be said to be well understood.

ACKNOWLEDGMENTS

We would like to thank Professor A. G. Redfield for sending us a copy of his work before publication. We would also like to thank R. Leisure for help in sample preparation and data taking.

[14] We wish to thank Dr. H. Kessemeier for making this measurement.