

Nuclear Magnetic Resonance Saturation in Lithium

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The real part χ' of the rf nuclear magnetic susceptibility was measured absolutely for applied rf fields between 0.001 and 5 G, at 77°K and 10.7 Mc/sec. Above the saturation level of 0.02 G the discrepancy between theory and experiment is less than 20%.

SEVERAL years ago it was observed¹ that the saturation behavior of the nuclear spin resonance in solids was radically different from that predicted by the Bloch equations or the theory of Bloembergen, Purcell, and Pound. It was found that the absorption and dispersion signals narrowed² and became Lorentzian on saturation and, more surprising, the dispersion χ' increased on saturation and showed no decrease until the rf field was comparable to the dipole-dipole interaction field. A theory of spin behavior was developed¹ which used as its starting point the idea of spin temperature in the coordinate system rotating with the rf field.³

Since then, the predictions of the spin temperature assumption have been tested and confirmed experimentally, under adiabatic conditions for which spin-lattice relaxation plays no role, in both the fixed and rotating frames of reference.³⁻⁶ The spin temperature assumption in the rotating frame implies that there is an ordering of the spins with respect to their local fields; recent experiments⁷ of Anderson and Hartmann have strikingly confirmed that this is so. These ideas have also been used in the analysis of double resonance techniques which are potentially useful for spectroscopy of low abundance spin species⁸ and for dynamic polarization.⁹

The theory of steady-state experiments, such as saturation measurements, is more complicated than that required for adiabatic experiments, since spin-lattice relaxation must be taken into account. Speculations concerning spin-lattice relaxation contained in the earliest work have been essentially confirmed in a general treatment¹⁰ which has been applied to this problem.¹¹ More recently, the spin temperature hy-

pothesis under steady-state conditions has been justified on more general grounds.¹² Several interesting experimental studies of steady-state saturation and double resonance saturation have been published,^{5,9,13-15} but of these only the experiment of Goldburg¹⁵ was performed under conditions readily permitting precise comparison between theory and experiment. His work shows excellent agreement for Na²³ in NaCl.

The present research was undertaken to provide a second quantitative test of the theory. Metallic lithium is a good material for such a test because its spin-spin interaction¹⁶ and spin-lattice relaxation^{17,18} have been extensively studied. Audio frequency absorption studies¹⁶ show that, for typical lithium samples, there is negligible quadrupole interaction and indirect electron coupled spin-spin interaction.

Our measurements were confined to the dispersion or real part of the rf nuclear magnetic susceptibility. The theory is applicable when $\gamma^2 H_1^2 T_1 T_2 > 1$ and it predicts^{1,11} that $\chi'' \ll \chi'$ and that

$$\chi' \equiv \frac{M'}{2H_1} = \frac{M_0 \gamma \Delta}{2[\Delta^2 + \gamma^2(H_1^2 + 2.2H_L^2)]}. \quad (1)$$

Here M' is the component of rf magnetization which is in phase with the applied rf field $2H_1 \cos \omega t$, H_0 is the dc field, M_0 is the equilibrium nuclear magnetization in H_0 , Δ is equal to $\omega - \gamma H_0$ and H_L^2 is the mean square local field in the rotating frame. H_L^2 is equal theoretically to one third the Van Vleck second moment of the unsaturated absorption line. The factor 2.2 multiplying H_L^2 is the ratio of the spin-lattice relaxation time at high dc magnetic field to that at zero field, measured¹⁸ at 4.2°K. This ratio is expected theoretically to equal the ratio of the relaxation rate for spin-spin

¹ A. Redfield, Phys. Rev. **98**, 1787 (1955).

² D. F. Abell and W. D. Knight, Phys. Rev. **93**, 940 (1954).

³ For an introduction to these ideas see C. P. Slichter and W. Holton, Phys. Rev. **122**, 1701 (1961); and W. Goldburg, *ibid.* **128**, 1554 (1962).

⁴ A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961) Chap. V.

⁵ A. Abragam and W. G. Proctor, Phys. Rev. **81**, 278 (1951).

⁶ I. Solomon and J. Ezraty, Phys. Rev. **127**, 78 (1962).

⁷ A. G. Anderson and S. Hartmann, Phys. Rev. **128**, 2023 (1962).

⁸ S. Hartmann and E. L. Hahn, Phys. Rev. **128**, 2042 (1962).

⁹ A. Landesman and M. Goldman (to be published); see also Compt. Rend. **252**, 263 (1961).

¹⁰ A. Redfield, I. B. M. Journal **1**, 19 (1957); see reference 4, Chap. VIII for other work in this area.

¹¹ Reference 4, Chap. XII, Sec. 2.

¹² A. Redfield, Phys. Rev. **128**, 2251 (1962).

¹³ N. Bloembergen and P. P. Sorokin, Phys. Rev. **110**, 865 (1958).

¹⁴ D. F. Holcomb, Phys. Rev. **112**, 1599 (1958).

¹⁵ W. Goldburg, Phys. Rev. **122**, 831 (1961).

¹⁶ A. G. Anderson, Phys. Rev. **115**, 863 (1959).

¹⁷ D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

¹⁸ A. G. Anderson and A. G. Redfield, Phys. Rev. **116**, 583 (1961). This paper and also reference 10 contain an important error. The factor 10/3 which occurs in equation 9 and subsequent equations should have been 5/3. One of us (A. G. R.) has recently remeasured the field dependence of T_1 in Li with improved accuracy at 1.4°K and finds reasonable agreement with theory using the factor 5/3 and the previous value of $\delta=2.2$. We wish to thank L. C. Hebel for pointing out this error.

energy to that for Zeeman energy, at 77°K.¹⁹ The latter ratio is important in determining the steady-state value of the dispersion signal.

Equation (1) is the prediction which we test in this research; it is expected to be valid if relaxation takes place via conduction electrons and there are no effects from diffusion or quadrupole interaction.

EXPERIMENTAL METHOD AND RESULTS

All the experiments described here were performed at a frequency of 10.7 Mc/sec and at a temperature of 77°K. At this temperature, relaxation due to diffusion is negligible. The sample was a commercially supplied lithium dispersion of the same quality used in previous research.^{16,18} We used two methods to measure χ' . For H_1 less than about 1 G the sample was placed in a stable crossed coil bridge immersed in liquid nitrogen and the nuclear signal was observed directly (i.e., without the usual audio modulation techniques) as we swept slowly through resonance. At higher rf fields microphonic noise forced us to use a long-pulse technique. In this technique the rf field was applied as a pulse long compared to T_1 , so that the spin magnetization reached its steady state by the end of the pulse. Under the conditions of these measurements, this steady-state spin magnetization consisted of a static z component less than M_0 , and a precessing transverse component which is presumably in phase with rf field and is equal to $M' = 2\chi'H_1$. This precessing component of magnetization was measured by cutting off the rf field in $\frac{1}{2}$ μ sec and measuring its free induction decay signal after the end of the pulse. The amplitude of this free precession signal is proportional to M' or χ' , so that this measurement is equivalent to a steady-state measurement of χ' . In this latter technique we were also able to infer H_1 from the length of a 180° pulse, and calibrate the sensitivity of our apparatus by applying a 90° pulse after reaching thermal equilibrium.

In this way we avoided the ambiguities involved in audio field modulation, and we also eliminated ambiguities of unknown calibration constants.

STEADY-STATE MEASUREMENT

A rigid miniature crossed-coil head, which had a sheet copper electrostatic shield between the transmitter and receiver coils designed to homogenize H_1 , was immersed in liquid nitrogen. Residual unbalance inside this head was cancelled by means of a small additional variable mutual inductance²⁰ placed externally in series with the ground returns of the transmitter and receiver coils, and also by feeding transmitter power to the receiver through an attenuator-phase shifter. While this latter combination alone could in

principle have furnished a complete null, the mutual inductance was useful for a first adjustment, and when it was so used microphonic noise was reduced.

The receiver was designed for pulse work, and will be described elsewhere.²¹ The transmitter was an ordinary signal generator. The output circuit of the receiver was a phase detector whose reference signal was derived from the transmitter through a phase shifter. To observe the dispersion signal we adjusted this phase shifter either for minimum microphonic noise or to give no response when the additional mutual inductance was varied. The output of the phase detector was recorded while the magnetic field was swept. Field sweep was accomplished by connecting a modified²² Tektronix ramp generator to the sweep input of the magnet current regulator.

At high rf levels this apparatus was plagued with erratic noise, presumably microphonics due to nitrogen bubbling. Only by waiting impatiently could we take data at these levels. This noise also prevented us from observing the absorption mode.

At 77°K the bridge balance was slightly field dependent, possibly due to Hall effect in the lithium. As a result there was a slight baseline tilt in the dispersion recordings, but the resulting errors in data presented below is estimated to be about 2% and thus negligible.

The rf field was measured using a pulse transmitter,²³ and using the receiver as an amplitude detector. The transmitter pulse length was adjusted to give no free induction tail after the pulse; this pulse was assumed to be a 180° pulse having a length $\pi/\gamma H_1$ sec, from which H_1 was determined. Unfortunately, this calibration was performed with a relatively feeble pulse transmitter for which a 180° pulse had a length of 35 μ sec, so that H_1 was not much greater than the dipole-dipole interaction field. Under these conditions it is not certain that the transverse magnetization will be null at a time $\pi/\gamma H_1$ sec after the start of the pulse, though we think that the error in this assumption is small. The rf field at other levels was determined from the voltage across the transmitter coil; precautions were taken to avoid errors due to harmonic content in the rf waveform.

LONG PULSE MEASUREMENTS

At high power levels, noise prevented use of the steady-state technique, and instead we measured the amplitude of the free induction decay after a pulse long compared to the spin lattice relaxation time. This method is similar to those used by Sorokin and Bloembergen¹³ and by Goldburg,¹⁵ and has the advantage that it is completely free of microphonic noise. The method measures $(\chi'^2 + \chi''^2)^{1/2}$ but at high power levels it is known that χ'' is negligible, so that χ' is what was really measured.

¹⁹ This statement follows easily from a theoretical analysis based on reference 11. These ratios are expected to be temperature independent if relaxation is due to conduction electrons alone.

²⁰ R. J. Blume, Rev. Sci. Instr. (to be published).

²¹ R. J. Blume (to be published).

²² R. J. Blume, Rev. Sci. Instr. **32**, 743 (1961).

²³ R. J. Blume, Rev. Sci. Instr. **32**, 554 (1961).

At 77°K, the spin lattice relaxation time is about $\frac{1}{2}$ sec. Pulses 3 sec long were applied repetitively by the pulse transmitter. The receiver recovered in less than 5 μ sec, and its phase detector reference voltage was derived from the transmitter crystal oscillator, which ran continuously. Thus the free induction decay was coherently detected by the receiver phase detector. The output of the phase detector was fed to a "boxcar" sampling integrator,²⁴ which sampled the signal for a 10- μ sec interval, starting at a standard delay of 9.5 μ sec after the end of the pulse. The output time constant of this circuit was such that it averaged over several successive free induction decays. The output of the boxcar sampling circuit was recorded as the dc field was swept. The same head, transmitter, receiver, rf field calibration, and dc field sweep arrangement were used as in the steady-state measurement.

During the rf pulse the spins are driven in phase with the rf field. When the rf is cut off, however, their free precession rate is determined by the value of the dc field. When the dc field is off resonance, they will precess at a different frequency than that of the continuously running transmitter crystal oscillator²³ which provides the reference voltage to the phase detector, and a beat modulation will appear on the free induction signal at the phase detector. Thus if the phase of the reference is properly adjusted near resonance to detect the free induction decay, then as the field is swept off resonance, for finite delay after the pulse, a correction must be made for this beat modulation. We corrected for this dephasing by repeating our runs with the phase detector reference shifted by 90°. The final data used were the square root of the sum of the squares of the two runs, and thus presumably were a true indication of the amplitude of the precessing magnetization. The runs taken with a 90° phase shift showed slight asymmetries and resonance shifts which did not seem to be associated with phase misadjustment or residual absorption. We do not understand the origin of these effects. The correction for dephasing resulted in an increase of about 20% in our linewidth and peak to peak signal, relative to those inferred from uncorrected data.

We calibrated the sensitivity of our apparatus by flipping the full magnetization M_0 with a 90° pulse after thermal equilibrium was reached, and sampling the resulting free induction decay with the boxcar circuit using the same standard delay after the pulse and the same sampling time as in the measurements above. This measurement was repeated with various lengths of 90° pulses down to 6.5 μ sec, adjusting the amplitude of the pulse appropriately and keeping the boxcar delay after the end of the pulse constant. The signal amplitude extrapolated to a zero-length 90° pulse was assumed to correspond to the full magnetization M_0 . This calibration procedure presumably empirically

measures the signal which would have been observed after an infinitesimally short infinitely large 90° pulse, at the standard delay and sampling time used.

The ratio of M' to M_0 is equal to the ratio of the free induction decay signal immediately after the end of a long pulse to the signal immediately after an infinitesimally short 90° pulse. In practice we measure or infer both signals at a later time, the same standard delay after the end of the pulse. Clearly no error will result from this delay if the free induction decay after an infinitesimally short 90° pulse has the same temporal form as the free induction decay after a pulse long compared to the spin lattice relaxation time. Readers familiar with the theory of saturation and free induction decay^{4,25} will recognize that the two decays

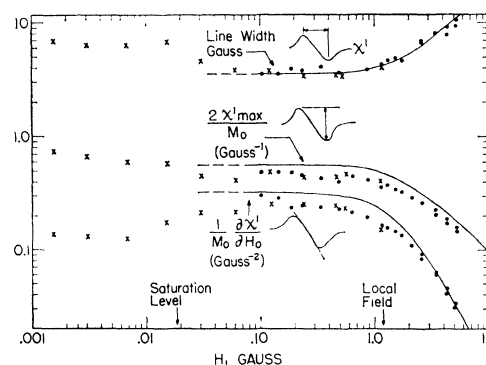


Fig. 1. Measured dispersion peak-to-peak amplitude and width, and dispersion derivative as a function of the rf amplitude. The solid circles are pulse data and the crosses are steady-state data normalized to agree with the pulse data (for χ_{\max}' and $\partial\chi'/\partial H_0$ only). Otherwise there are no adjustable parameters in either theory or experiment.

should have the same form if the saturated spin system is indeed described by a spin temperature in the rotating coordinate system. In any case any error so introduced would be small, since the average time of observation after the pulse (15 μ sec) is small compared to the transverse decay time ($\sim 50 \mu$ sec).

DATA

The observed dispersion curves showed the characteristic behavior described in the first paragraph. We have not analyzed our data in great detail to see if, for example, they are truly Lorentzian, but instead we simply measured the width between peaks of χ' , the peak to peak amplitude of χ' , and the slope $\partial\chi'/\partial H_0$ at resonance. These quantities are plotted in Fig. 1, together with theoretical curves. The pulse measurements are absolute measurements both in amplitude and rf field. The steady-state measurements of $\partial\chi'/\partial H_0$ and χ_{\max}' were not amplitude calibrated, so they have been plotted multiplied by an arbitrary constant to agree with the pulse measurements.

²⁴ R. J. Blume, Rev. Sci. Instr. **32**, 1016 (1961).

²⁵ I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).

The theoretical curves in Fig. 1 were obtained from (1) assuming that H_L^2 is equal to $\frac{1}{3}\langle\Delta H\rangle$, where $\langle\Delta H\rangle$ is the Van Vleck second moment of the unsaturated resonance absorption. Since $\langle\Delta H\rangle$ is dependent on crystal orientation, it is necessary to average over orientation. A precise average is complicated but we have estimated that an error of less than 1% is made in linewidth and peak to peak amplitude if we use (1) with $H_L^2 = \frac{1}{3}\langle\langle\Delta H\rangle\rangle$. Here $\langle\langle\Delta H\rangle\rangle$ is the Van Vleck second moment averaged over crystal orientation and is equal theoretically²⁶ to 5.5 G.² This value was used to obtain the upper two curves in Fig. 2 of reference 26. For $\partial\chi'/\partial H_0$ at resonance the orientation average correction is more complicated, and we estimate that an error of less than 1% will be made if we use (1) to calculate $\partial\chi'/\partial H_0$ at resonance, setting $H_L^2 = (0.97) \times \frac{1}{3}\langle\langle\Delta H\rangle\rangle$. The lower theoretical curve in Fig. 1 was obtained in this way.

DISCUSSION

The agreement between theory and experiment is qualitatively convincing; the theory works well for H_1

²⁶ H. W. Gutowsky and B. R. McGarvey, *J. Chem. Phys.* **20**, 1472 (1962).

as small as $\frac{1}{10}$ of the local field. We estimate the systematic error in the experiment at less than 10% in signal and H_1 , and negligible in H_0 and linewidth. Thus there is a minimum discrepancy of 10% between theory and experiment.

Some possible theoretical factors which might explain the small discrepancies are incorrect assumptions concerning transverse and spin-spin energy relaxation, or quadrupole effects. From an experimental point of view we may have overlooked some defect in our calibration procedure.

The theory embodied in (1) is only supposed to be applicable above saturation; thus the theoretical curves in Fig. 1 are drawn only in this region. Provotorov²⁷ has recently advanced a plausible theory applicable through the entire saturation region assuming only $H_1 \ll H_L$ and $1/T_1 \ll \gamma H_L$. Thus this theory should bridge the gap down to small H_1 in the present experiment. We have not attempted to compare his theory with our data, but there seem to be no striking discrepancies. Above saturation Provotorov's theory agrees with the theory of reference 1.

²⁷ B. N. Provotorov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **41**, 1582 (1961) [translation: *Soviet Phys.—JETP* **14**, 1126 (1962)].

Size-Dependent Spin Relaxation Time

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The increase of the paramagnetic relaxation time due to the increase in size of the crystal of copper Tutton salt reported by Nash is interpreted from a model of Eisenstein.

IN a recent article, Nash reported that a "spin relaxation time" of copper Tutton salt crystal in the helium temperature region was size dependent.¹ This relaxation time is deduced from the recovery curve when the spin system is removed from a saturation magnetic field. In this paper we propose to explain this observation by a model of Eisenstein.² An anomalous dispersion of some paramagnetic salts³ will also be explained.

Eisenstein has modified the thermodynamical approach of Casimir and Du Pr e⁴ with two assumptions: there is a finite specific heat of the lattice and a local distribution of the spin temperature. The dispersion function of the complex susceptibility χ^* is then given by,

$$\frac{\chi^* - \chi_\infty}{\chi_0 - \chi_\infty} = \frac{s}{1 + isx} + \frac{3}{R^2} (1-s) \frac{\lambda r_0 \coth \lambda r_0 - 1}{x(1 + isx)^2}, \quad (1)$$

where $s = C_L / (C_H + C_L)$, with C_H and C_L the specific heat of the spin (at constant field) and of the lattice, respectively; $R^2 = r_0^2 C_L d / K s \rho$. K is the thermal conductivity, r_0 is the radius of the (spherically shaped) crystal, d is the molar density, $\rho / 2\pi$ is the spin-lattice relaxation time,

$$\lambda r_0 = R \left(\frac{1 + isx}{1 + ix} \right)^{1/2}, \quad (2)$$

and $x = \nu \rho$, with ν as the measuring frequency. Therefore, the frequency spectrum of the normalized complex susceptibility depends on two parameters, s and R . In the case of classical dispersion of Casimir and Du Pr e, $s = 1$ ($C_L = \infty$) and the second term in the right side of Eq. (1) is zero; therefore, there is no R dependence.

Equation (1) has been computed numerically for

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¹ F. R. Nash, *Phys. Rev. Letters* **7**, 59 (1961).

² J. Eisenstein, *Phys. Rev.* **84**, 548 (1951).

³ J. van den Broek, L. C. van der Marel, and C. J. Gorfer, *Physica* **25**, 371 (1959).

⁴ H. B. G. Casimir and F. K. Du Pr e, *Physica* **5**, 507 (1938).