Detection of NMR Using a Josephson-Junction Magnetometer*

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Nuclear magnetic resonance has been detected by following changes in the steady-state value of the longitudinal magnetization with a Josephson-junction magnetometer. Unlike previous fast-passage detection methods, this mode of detection gives a signal amplitude of $2M_0$ independent of the resonance linewidth and the rf power level. Maximum-intensity signals from room-temperature LiF have been obtained at 40 dB less power than that required for maximum signal using conventional adiabatic fast-passage detection methods.

A new method of detecting nuclear magnetic resonance has been developed. Changes in the steady-state value of the longitudinal magnetization induced by adiabatic fast passage have been detected with a Josephson-junction magnetometer.[1] Unique to this detection method is the ability to detect broad NMR lines at full intensity using low levels of rf power. The nuclear magnetic resonances of protons in water as well as Li^7 and F^{19} nuclei in room-temperature LiF powder have been detected with this technique. The broad signals of LiF were detected at full intensity using 40 dB less rf power than required by conventional detection. This technique should find application in isotope trace analysis in solids, in geological dating, in thermometry, in the study of broad nuclear magnetic resonance lines in biological molecules, and possibly in the study of chemical shifts in solids.

Adiabatic fast passage carried out using a frequency sweep causes a total change in the longitudinal magnetization of twice the steady-state value M_0. The steady-state value of the magnetization is equal to $\chi_0 H_0$ in the unchanging dc field H_0. The static susceptibility χ_0 is 3.22×10^{-10} (cgs) for protons in water at 25°C and slightly less for Li^7 and F^{19} nuclei in LiF powder. This change of $2M_0$ in M_z has been detected in a 7.47-kOe field using a superconducting pickup coil coupled to a Josephson-junction magnetometer.

Prior to this experiment, adiabatic fast passage has been detected by following the transverse magnetization with an rf coil perpendicular to the applied dc field. A pulse was observed as the magnetization swung past the rf coil on its way toward inversion. The magnitude of this pulse was reduced by the factor $H_1/\delta H$ for a broad line of width δH because of the dephasing of the spins in the transverse direction. The only way to overcome this incoherence was to increase the amplitude (H_1) of the rf field.

In the present method of detection, the signal amplitude is $2M_0$, independent of the linewidth and rf power level as long as the conditions of adiabatic fast passage are met. These conditions are[2]

$$|\gamma H_1|^2 \underset{\text{adiabatic}}{\gg} \frac{d\omega}{dt} \underset{\text{fast}}{\gg} \max\left(\frac{\gamma H_1}{T_1}, \frac{\gamma H_L}{T_1}, \frac{\gamma \Delta H}{T_1}\right).$$

The additional condition $1/T_2 \cong \gamma H_1$ holds for solids where $T_2 \ll T_1$. Here γ is the gyromagnetic ratio of the spins, H_1 the rf field amplitude, ω the radio frequency, T_1 the longitudinal relaxation time of the spins, T_2 the transverse spin relaxation time, H_L the local field in a rigid lattice, and ΔH the inhomogeneity of the dc magnetic field. For this type of experiment, which uses a pickup coil sensitive to changes in M_z, the dc magnetic field is held absolutely constant. The sweep through resonance is performed by sweeping the radio frequency.

The experimental configuration consists of a 0.25-cm^3 cylindrical sample holder containing an rf coil whose axis is perpendicular to that of the sample cylinder. The sample holder is located in a room-temperature Dewar finger. This Dewar finger is surrounded by a type-II superconducting pickup coil coaxial with the sample and coupled to a Josephson-junction magnetometer. A type-II superconducting persistent-mode solenoid coaxial with the sample supplies the stable field of 7.47 kOe.

The result of an adiabatic fast-passage experiment performed on protons in water is shown in Figure 1. This trace is a superposition of sweeps in opposite directions through resonance. For this curve the fast-passage conditions are as follows:

$$|\gamma H_1|^2 > d\omega/dt > \gamma \Delta H/T_1 ,$$

$$3.2\times10^6/\text{sec}^2 > 0.84\times10^6/\text{sec}^2 > 0.21\times10^6/\text{sec}^2 .$$

The linewidth appears as the distance between

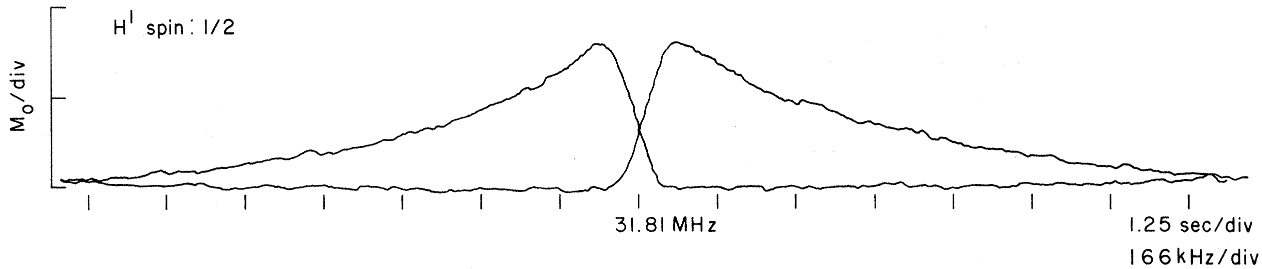

FIG. 1. Adiabatic fast passage through the nuclear magnetic resonance of protons in water at 25° C in a magnetic field of 7.47 kOe. This trace is a superposition of passages in each direction. The ordinate is labeled in units of the equilibrium magnetization of the protons in the applied field.

rise points of the opposing sweeps. The broad line is due to the magnet's field inhomogeneity over the sample, which was measured with a Hall probe to be 3.1×10^{-3}. The rise slope in each direction depends on the distribution of Larmor frequencies arising from this field inhomogeneity. The longitudinal spin relaxation time (T_1) of the protons in water is apparent as the exponential decay from maximum signal in either direction. This trace gives a value of 3.5 ± 0.4 sec, consistent with the known value. The crossover point of the opposing sweeps yields a resonant frequency of 31.81 ± 0.005 MHz, consistent with the field of 7.47 kOe measured by the Hall probe.

The ordinate of the trace is calibrated in units of the equilibrium magnetization M_0 of protons in water at 25°C in the applied field. The output of the Josephson-junction magnetometer was read as the empty sample holder at 25°C was inserted into the superconducting pickup coil with the magnet charged to 7.47 kOe. This signal was subtracted from a similar curve taken as the water-filled sample holder was inserted. These data, in conjunction with the known value of 0.72×10^{-6} (cgs) for the diamagnetic susceptibility of water at 25°C, calibrated the output of the Josephson-junction magnetometer in cgs units of susceptibility. The signal does not reach the predicted value of $2M_0$ because of imperfect rf coil geometry and a slow scan rate. More rapid scanning of the resonance was ruled out by the time response of the eddy-current shielding in the Dewar walls between the sample and the pickup coil.

It should be possible to reverse the calibration procedure described above and use the well-known nuclear susceptibility to calibrate the units of static susceptibility which are uncertain at present.[3]

The results of adiabatic fast-passage experiments on a very pure sample of powdered LiF[4] are shown in Fig. 2. The top trace shows a single passage through the Li^7 line under the conditions

$$|\gamma H_1|^2 \gg d\omega/dt \gg \gamma\Delta H/T_1 ,$$

$$3.3\times10^5/\mathrm{sec}^2 \gg 2.6\times10^4/\mathrm{sec}^2 \gg 69/\mathrm{sec}^2 .$$

The bottom trace is that of a single passage through the F^{19} line with

$$|\gamma H_1|^2 \gg d\omega/dt \gg \gamma\Delta H/T_1 ,$$

$$1.0\times10^6/\mathrm{sec}^2 \gg 1.0\times10^5 \gg 2.8\times10^2/\mathrm{sec}^2 .$$

In each case the linewidth appears as the distance between the rise point and the point of maximum signal. The linewidth is due to the magnet inhomogeneity of 23 G. The known local field of LiF is approximately 8 G. The midpoints of the rise slopes of these traces correspond to resonant frequencies consistent with the 7.47-kOe dc field. The ordinate of each trace has been calibrated

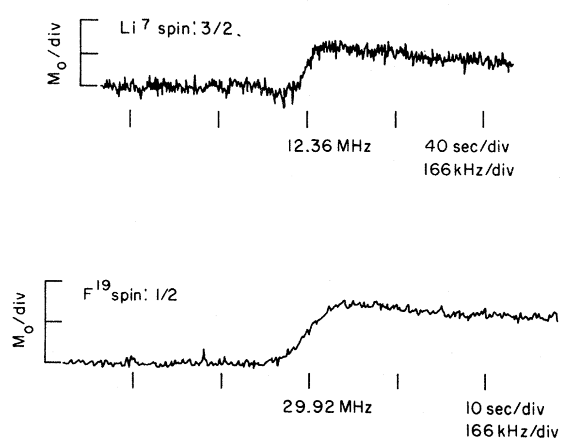

FIG. 2. Adiabatic fast passage through the nuclear magnetic resonances of Li^7 (top) and F^{19} (bottom) in a powdered sample of LiF at 25°C in a magnetic field of 7.47 kOe. The ordinate is labeled in units of the equilibrium magnetization of the respective nuclei in the applied field.

against the bulk susceptibility of water as described previously. The number density of each nucleus was found using the measured density of the given powdered sample. Loss of signal from the expected value of $2M_0$ is due to imperfect rf coil geometry resulting in an unwanted longitudinal rf field component over a portion of the sample volume.

The longitudinal relaxation time T_1 of either nucleus is long compared with the time scale of the trace as shown by the lack of decay of signal (S) from its maximum value. The relaxation time was measured by taking a trace after waiting a long time compared with T_1. This trace was followed by a second taken taken a time t later. The process was repeated and the points $\ln[1 - S(t)/S(0)]$ were plotted against t to find T_1. The value of T_1 for Li^7 was found to be $(3.5\pm0.5)\times10^3$ sec while for F^{19} it was $(2.1\pm0.3)\times10^3$ sec.

The striking feature of these data is that maximum signals have been obtained at power levels more than 40 dB down from the rf power required to yield maximum signal using conventional detection. That is, lines 8 G wide have been detected at full intensity using approximately 50 mG rf amplitude. With conventional detection of the transverse pulse the signal would have been reduced by $50\times10^{-3}/8$ under these conditions.

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[1]J. E. Zimmerman and H. A. Silver, Phys. Rev. 141, 367 (1966).

[2]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford Univ. Press, Oxford, England, 1961), pp. 34–46, 65–66. The right-hand inequality includes all sources of line broadening to ensure that the entire line is swept rapidly compared with T_1.

[3]P. W. Selwood, *Magnetochemistry,* (Interscience, New York, 1956), pp. 85–87.

[4]Used as supplied by Ventron Corporation, Beverly, Massachusetts, who state that Fe, Mn, Ni, Co, Cu, Zn, and Pb are each present at less than 0.5 parts per million.

Observations on the Escape of Negative Ions from Pressurized, Turbulent He II†

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Data on the capture and escape of negative ions in turbulent He II are reported for various pressures. The results are consistent with a revised version of Vinen's dimensional theory and previous experimental results on rotating He II. A model for vortex annihilation is developed which allows the turbulence theory to be expressed in terms of a single dimensionless constant which we measure.

The suggestion by Onsager[1] that rotating He II is permeated by a linear array of quantized vortex lines, each with circulation $\kappa = h/m_{\rm He}$, and the first experimental evidence for quantized vorticity in rotating helium[2] led Vinen[3] to propose a physical basis for the Gorter-Mellink mutual friction force.[4] Following Feynman,[5] he proposed that turbulent He II was penetrated by an irregular array of lines and that mutual friction was the result of interactions between this vorticity and the normal fluid. Assuming isotropic and homogeneous turbulence, a single parameter L_0, the equilibrium line length in unit volume, is sufficient to describe the structure. L_0 is determined by the rates of growth $\dot{L}_g$ and decay $\dot{L}_a$ of vorticity. Growth is analogous to the dynamical expansion of a vortex ring, larger than a certain critical radius, in a two-fluid counterflow, and decay follows from a speculation[5] that two lengths of vortex line with oppositely directed circulation