

Spin-Lattice Relaxation Below 1K

J. S. Waugh, P. C. Hammel, P. L. Kuhns and O. Gonen

*Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139 USA*

Contents

| | |
|---|-----|
| I. Introduction | 97 |
| II. Relaxation by Helium-3 at Surfaces | 98 |
| III. Possible Direct Measurements of Spin Diffusion | 99 |
| IV. Prospects for the Future | 101 |
| V. References | 101 |

I. Introduction

NMR experiments at very low temperatures have been carried out for a long time, generally not as a general purpose method for analyzing structure and dynamics but rather as a convenient diagnostic tool in the study of substances whose special properties at very low temperatures are of interest. These include most prominently solid hydrogen and solid and liquid helium-3.

It must always have been obvious that the "routine" applications of NMR would often benefit from the use of low temperatures. The most obvious reason is the greatly enhanced sensitivity which in principle can be obtained; NMR is ordinarily spectacularly insensitive because the Zeeman levels involved are separated only by a very small energy difference $\hbar\omega_0$, yet at ordinary temperatures $\hbar\omega_0/kT$ is so small that the levels are almost equally populated and the excess of absorption over stimulated emission is very small. The manner in which this situation improves with lower temperatures is indicated in Figure 1, where we have chosen the particular case of protons with $\omega_0/2\pi = 144$ MHz as an example. Three features are evident from the figure: 1) a gain in sensitivity of $10^4 - 10^5$ ($10^8 - 10^{10}$ in terms of power sensitivity or averaging time) is

available at the lowest temperatures. 2) A point of diminishing returns is reached at temperatures of a few millikelvin where $\hbar\omega_0 \simeq kT$, meaning that one need not be concerned about the difficult technology for reaching temperatures lower than that; fortunately helium dilution refrigerators, capable of reaching the millikelvin regime, are now commercially available. 3) If one's goal is higher sensitivity it is foolish to stop at, say, the easily reached boiling point of helium since only a tiny fraction of the potential improvement is realized at that point.

Why has such high sensitivity NMR not been developed long since? The answer is in part that the necessary cryogenic techniques have not usually been familiar to experts in NMR spectroscopy. However the principal reason is certainly connected with the fact that spin lattice relaxation times of insulators tend to become astronomically long at low temperatures (1); it may be possible to cool the lattice but the spins remain relatively hot and the hoped-for gain in sensitivity is not achieved.

In this respect hydrogen and helium-3 are exceptional substances, each for its own reason. That being the case it is worth wondering whether advantage might be taken of their relatively rapid relaxation to produce polarization of other species of

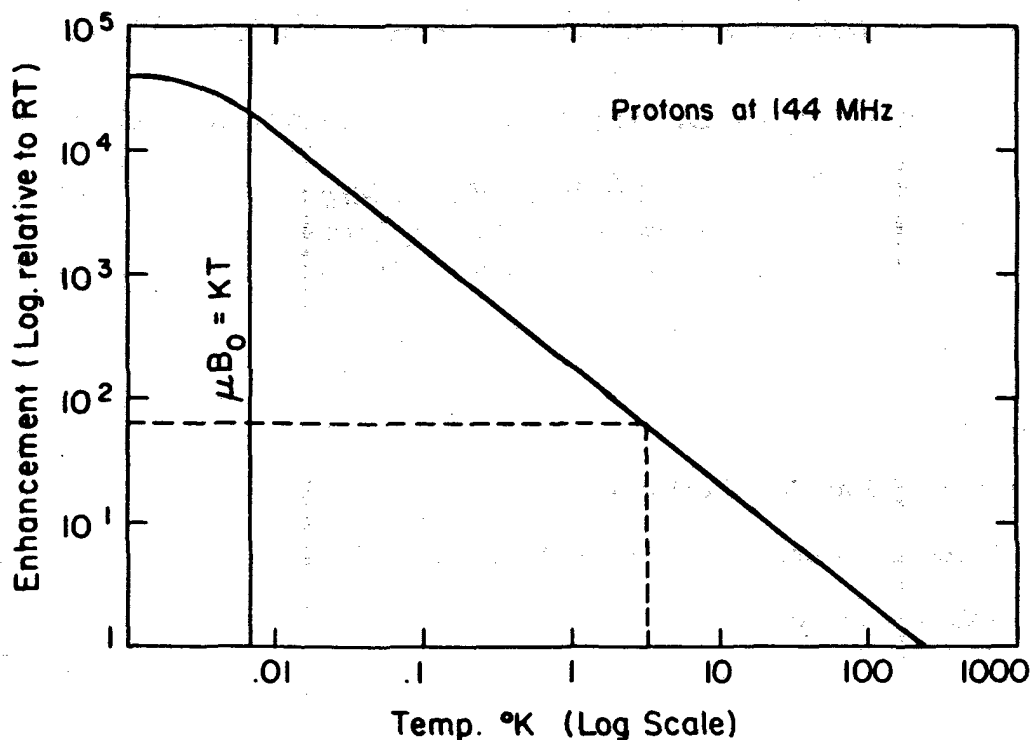


Figure 1. Predicted dependence of NMR voltage sensitivity on temperatures for protons in a field of 3.4T.

perhaps broader interest. One possibility is to isolate a small molecule of interest in a rare gas matrix which also contains some hydrogen, by deposition of molecules of a gas mixture on a very cold surface. Polarization might then be transferred from the hydrogen to the molecule of interest, for example by cross-polarization technique. Indeed preliminary studies of this kind have been carried out and are continuing but we will not discuss them further here.

II. Relaxation by Helium-3 at Surfaces

The breakthrough which led to most of the current activity in millikelvin NMR involves helium-3 instead. It was discovered by Friedman, Millet and Richardson (2) that liquid ^3He not only relaxes reasonably rapidly but a) does so at the surfaces of solids and b) in doing so spontaneously relaxes nuclei of other species (in their case ^{19}F in $(\text{CF}_2)_n$) at the surface. The resulting surface relaxation rate is found experimentally to be independent of temperature (suggesting the importance of tunneling dynamics) and (approximately) inversely proportional

to the external field B_0 . The reasons for this rather unusual field dependence are not yet entirely clear; each laboratory tends to have its own private view of the situation. In the simplest view, the field dependence of the surface relaxation rate is simply a map of the spectral density of fluctuations of the dipole-dipole interactions responsible for the relaxation. For the simplest processes in bulk, such spectral densities are approximately Lorentzian in shape. However when the motion occurs in two dimensions the spectral densities tend to depart from Lorentzian in the directions seen experimentally for the ^3He surface relaxation phenomenon.

Whatever the mechanism, the surface relaxation phenomenon does seem to work. We have observed it for ^1H , ^2H , ^{13}C , ^{29}Si and three isotopes of Sn where the characteristic surface relaxation times range from a few seconds to a few hours, depending on the gyromagnetic factor of the relaxed species and its proximity to the surface. Thus the utility of the Friedman, Millet, Richardson phenomenon can be said to have been demonstrated.

Of course this leaves open the question of relaxation of nuclei in the bulk. Assuming that intrinsic T_1 's are astronomically long, the only path open is by spin diffusion (3). By this is meant the process

by which the nuclear magnetization becomes spatially uniform through mutual flip flops of neighboring spins brought about by the dipole-dipole interaction. We have seen evidence for this in studies of ^{29}Si in silica. When the particle size is very small (70 Å) the relaxation is approximately exponential with a time constant of a few hours. When the average particle size is increased to 1–2 μm , where the surface spins provide only a very small fraction of the maximum observable signal, the magnetization grows much more slowly and as $t^{1/2}$. This is exactly what is expected for a diffusion law in the time regime where the penetration depth is still rather small. There the diffusion constant is estimated to be of the order of 10^{-15} cm^2/s .

III. Possible Direct Measurements of Spin Diffusion

The value of D estimated for ^{29}Si in SiO_2 is extremely small by comparison, for example, with the value of about 10^{-5} for actual molecular diffusion in liquid water. Even in solids with a much higher density of spins (^{29}Si is only 4% abundant) and with higher gyromagnetic factors, D is still expected to be very small – say, 10^{-12} cm^2/s for ^{19}F in CaF_2 . The slowness of spin diffusion is responsible for the fact that no really definitive measurements of it have yet been performed. Most experiments have involved measurements of T_1 in crystals containing paramagnetic impurities. It is imagined that rather rapid relaxation occurs for ^{19}F spins near the impurities, and under suitable conditions the overall T_1 is bottlenecked by spin diffusion between these impurities and remote spins in the bulk. There are difficulties in interpreting such measurements. First a necessarily random distribution of relaxation sinks poses a difficult boundary value problem for the diffusion equation. More importantly, efficient spin diffusion depends on an elementary step in which two neighboring spins perform a mutual flip-flop. This occurs in an energy conserving and therefore efficient manner only if the two spins have the same Larmor frequency. However spins near an impurity suffer shifts and splittings of their resonance, so that for example nearest-neighbor and next nearest-neighbor spins are likely to have different Larmor frequencies, imposing a “diffusion barrier” which is very difficult to assess or evaluate.

It was with these thoughts in mind that we attempted a direct “tracer” measurement of diffusion. The experimental setup is briefly as follows: A thin single crystal (or several crystals) of CaF_2 is immersed in liquid ^3He , and the ^{19}F resonance is initially saturated with a train of weak rf pulses bringing the ^{19}F system to effectively infinite spin temperature. At the surface however the ^{19}F spins come rapidly into contact with the ^3He bath, at, say, 10 mK. With the passage of time spin diffusion brings the interior of the crystal toward the same spin temperature. The situation is indicated schematically in Figure 2 where the magnetization profile is qualitatively indicated at two different times. At any time the area under the curve, measurable from the amplitude of the ^{19}F FID induced by a weak pulse, is proportional to $t^{1/2}$. An experimental measurement corresponding to this law, with suitable calibrations, then provides a direct *macroscopic* measurement of D . The experiment is made practical by the use of very low temperatures for two reasons: one is the high sensitivity with which a shallow surface layer can be detected owing to the improved Boltzmann factor, the other is the expected astronomically long values of T_1 in the bulk, which would otherwise cause a growth of magnetization of the entire sample and limit the total time over which the experiment could be carried out.

This seemingly straightforward experiment in fact failed; the magnetization did not grow according to the expected $t^{1/2}$ law and moreover its rate of growth depended on temperature, whereas neither the surface relaxation effect nor spin diffusion has any temperature dependence. We were forced to the conclusion that there is indeed a bulk T_1 mechanism many orders of magnitude more efficient than previous wisdom would have predicted at the lowest temperatures.

The principal basis for the aforementioned conventional wisdom is very simple. It is imagined that paramagnetic impurities are at the root of the T_1 process. Electronic spins are imagined to have some moderately efficient relaxation mechanism themselves. The electronic spin flips provide randomly fluctuating magnetic fields at neighboring nuclei, and these fluctuating fields are responsible for the nuclear relaxation. There are several mechanisms by which the electronic spins can in fact relax, each having its own characteristic dependence on

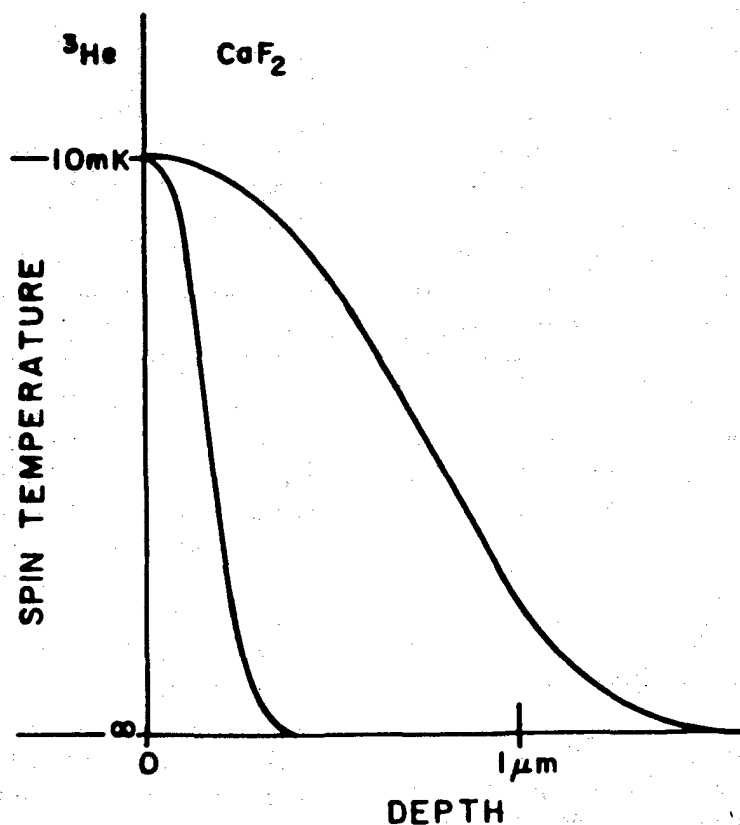


Figure 2. Expected development of magnetization (inverse spin temperature) profiles for a crystal where surface is clamped at the temperature of a ^3He bath (10 mK). The right-hand curve corresponds approximately to the situation in CaF_2 one hour after initial saturation of the ^{19}F resonance.

temperature and/or magnetic field strength. However there is another aspect of nuclear relaxation which does not depend on the details of the mechanism. It arises from the fact that the fluctuations of electronic magnetization at equilibrium are governed by the principle of detailed balance; the rates of upward and downward electronic spin flips must be such as to maintain the electronic system and thermal equilibrium (1). The electrons have very much higher values of Larmor frequency ω_e than the nuclei, and for them $\hbar\omega_e \simeq kT$ at around 1K. At, say, 10 mK the Boltzmann factor for the electrons then become roughly e^{-100} or 10^{-40} , this factor requiring a reduction in nuclear spin lattice relaxation rate by the same order of magnitude. Obviously at the lowest temperatures this exponential dependence on B_0/T completely overwhelms other details of the mechanism and renders a nuclear relaxation process moot in the millikelvin regime. This situation is illustrated in Figure 3 which refers to the lowest temperature T_1 measurements of which we are aware (4). The authors fit their results (obtained

over the range outlined by \square) to an expression of the form

$$T_1 = \text{const} \left(\frac{B_0^2}{T} \right) e^{+1.14 B_0/T}$$

which indeed contains something resembling a Boltzmann factor. Note that extrapolation of this law to low temperatures predicts the a value of T_1 approaching the age of the universe.

The same figure shows some of our measurements on CaF_2 crystals less heavily doped with paramagnetic impurities than those of Beal and Hatton (5). Note that at "moderate" temperatures our results are not so different from those of Beal and Hatton, but as the temperature is lowered toward 10 mK the relaxation time grows far less rapidly than expected, and in the neighborhood of 10 mK is perhaps 10^9 shorter than predicted. This phenomenon remains a considerable puzzle (6). It would be very interesting to carry out further experimental studies, for example of crystals with different and known concentrations of defects, etc. How-

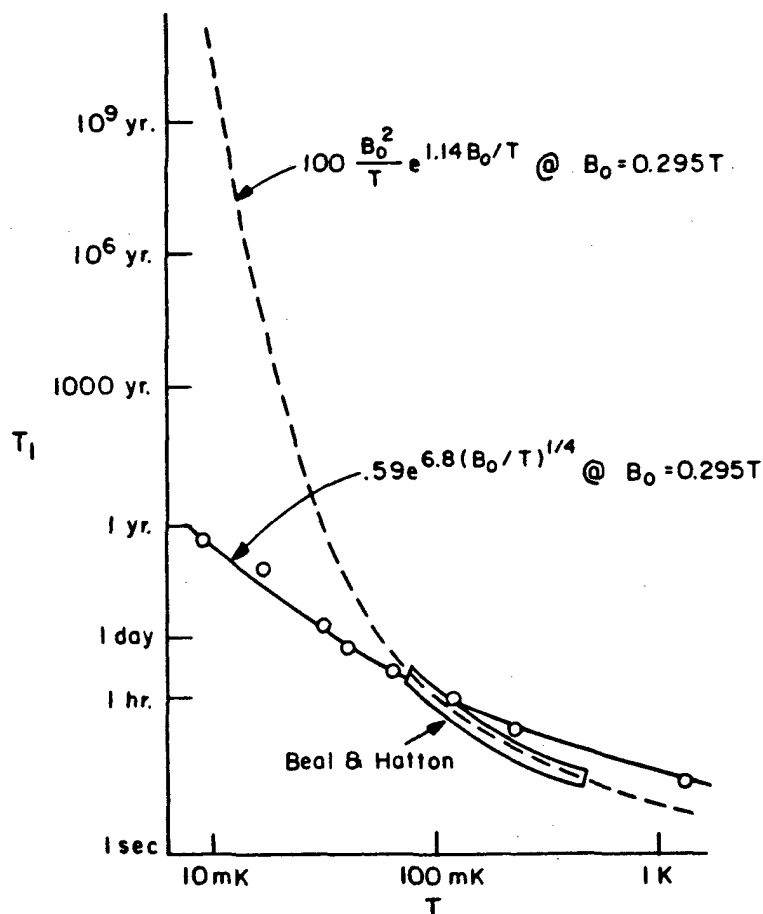


Figure 3. Experimental results on temperature dependence T_1 in CaF_2 . The open circles refer to measurements in our laboratory at a Larmor frequency of 12 MHz (5). The dashed line represents the fit reported by Beal and Hatton (4) to measurements on heavily doped CaF_2 . The fit has been adjusted to a Larmor frequency of 12 MHz for comparison with our results. The segment from approximately ~ 70 mK to approximately ~ 0.4 K indicated by a box indicates the actual measurements of Beal and Hatton.

ever note from the figure that the relaxation times are extraordinarily long so the experiments would be extremely laborious and are not likely to be done.

IV. Prospects for the Future

It is now well established that high sensitivity NMR is practical at very low temperatures because of the apparently universal mechanism produced at surfaces immersed in liquid ^3He . Bulk relaxation is more rapid than theoretically expected but still far too slow to be of practical interest. Spin diffusion is also so slow that relaxation of bulk solid through that mechanism is also impractical unless it is very finely divided. We are therefore left with a situation in which nuclei at or near surfaces exclusively are available for study. This obviously leaves open a variety of investigations in which it is in fact the properties of surface species which are of interest.

Sensitivity is so high that signals from a very small fraction of one monolayer of adsorbed molecules are easily detected. It is therefore likely that the considerable power of NMR in studying geometrical and electronic structure can be brought to bear in a more powerful way than heretofore in the fields of adsorption and catalysis. It is in this direction that most of our current effort is now aimed.

V. References

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⁶Since these lectures were presented, a new mechanism has been proposed which may account for the shortness of T_1 at very low temperature (J. S. Waugh and C. P. Slichter, *Phys Rev.* **B37**, 4337 (1988)).