PHYSICAL REVIEW B VOLUME 35, NUMBER 10 1 APRIL 1987

Unexpectedly rapid ^{19}F spin-lattice relaxation in CaF$_2$ below 1 K

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(Received 10 November 1986)

The spin-lattice relaxation time T_1 of ^{19}F in undoped CaF$_2$ single crystals was measured at temperatures T between 0.010 and 1.2 K in field strengths B_0 from 0.15 to 1.1 T. At the lowest temperatures T_1 was found to be orders of magnitude shorter than expected on the basis of previous experiments (at higher temperatures) and theories. The results fit the empirical expression $1/T_1 = 1.7\exp[-6.8(B_0/T)^{0.26}]\ \text{sec}^{-1}$. The mechanism of the relaxation is unknown.

INTRODUCTION

It is generally accepted that relaxation of nuclear Zeeman energy in pure rigid insulating crystals cannot occur through direct interaction between the nuclear spins and the lattice degrees of freedom.[1] The relaxation actually observed is always ascribed to the presence of electronically paramagnetic impurities, which serve as intermediaries between nuclear spins and lattice. The nuclei may relax with a single value of T_1 even when the impurities are rather dilute because a uniform nuclear Zeeman temperature is maintained through spin diffusion.[2] Since the spin diffusion is inherently independent of magnetic field B_0 and temperature, observed dependence of T_1 on these quantities must be understood (to oversimplify slightly) in terms of the level structures and relaxation properties of the paramagnetic centers themselves.

Electronic relaxation and its consequences for nuclear relaxation has been studied extensively, both theoretically and experimentally. A wide variety of behavior has been observed (and explained) for various types of impurities and various regimes of B_0 and T.[3-6] However one general feature invariably becomes dominant at temperatures low enough that the impurities are highly polarized. Then the effective rate of electronic flips (which generate the fluctuating fields needed to relax nearby nuclei) becomes reduced through detailed-balance considerations. The effectiveness of this quenching is measured roughly by a Boltzmann factor $e^{-\epsilon/kT}$, where ϵ is a characteristic level spacing of the impurity center: this factor is expected to dominate all other effects when the temperature is sufficiently low. For example a center with magnetic moment of one Bohr magneton in $B_0 = 1$ T has $e^{-\epsilon/kT} = 7\times10^{-30}$ at 0.01 K. Accordingly we are inclined to expect astronomically large values of T_1 in the millikelvin regime.

Most previous experimental studies have not extended to sufficiently large B_0/T to test this expectation. The lowest-temperature work of which we are aware is that of Beal and Hatton[7] in highly impure CaF$_2$, extending to a maximum B_0 of 0.115 T and minimum temperature of 70 mK, at which point a one-magneton moment would give $e^{-\epsilon/k_BT} \sim 10^{-3}$. Not surprisingly, the empirical formula to which they fit their results,

$$T_1 \simeq 100\frac{B_0^2}{T}e^{1.14B_0/T} \tag{1}$$

appears to contain a suitable magnetic Boltzmann factor. However their longest values of T_1 ($\sim$2 min) are still reasonably short. If (1) is extrapolated to, say $B_0 = 0.295$ T, $T = 0.01$ K (the reason for this choice to be made clear presently), we would expect $T_1 \sim 3\times10^{17}$ sec. A purer sample would presumably give a still larger value.

The present work began in an attempt to take advantage of this situation to measure the spin diffusion coefficient D and its anisotropy in single-crystal CaF$_2$. The notion, in brief, was to immerse the crystal in liquid ^{3}He, making use of the mechanism discovered by Friedman, Millet, and Richardson[8] to relax the surface ^{19}F spins to the temperature of the ^{3}He bath (10 mK). The ^{19}F resonance was initially saturated, and the growth of the total magnetization followed with time in a field of 0.295 T. After an initial period (of the order of a few days) during which this growth is controlled by the rate of surface relaxation, the magnetization M should grow as $(Dt)^{1/2}$, from which D can be determined. We were astonished to discover that the growth of M departed from this dependence. Moreover the rate of growth of M changed if the temperature was changed during an experimental run. Since both D and the rate of surface relaxation are independent of T,[2,9] the presence of a bulk T_1 mechanism is strongly indicated. We therefore redirected our effort to a study of the dependence of T_1 on B_0 and T.

EXPERIMENTAL METHOD

The relaxation measurements which we report here were made on four oriented single-crystal disks of CaF$_2$ approximately 7 mm in diameter and 0.4 mm thick, providing a total mass of 290 mg of CaF$_2$. The crystals had been grown by the Bridgman method and were claimed to have less than 1 ppm content of impurities.[10] ESR measurements (at 5 K and between $g = 0.7$ and $g = 5$) on the crystals revealed a weak signal near $g = 2.6$. [Both ESR and NMR measurements were made with a (100) axis parallel to the field.] These measurements do not provide a good quantitative measure of the impurity levels but indicate that they are between 0.1 and 1 ppm. Relaxation measurements were also made on a second CaF_2 sample obtained from another supplier,[11] which ensured that our results were not peculiar to the original samples. The crystal orientation in these experiments is not known. The T_1 values for the second sample at 11.8 MHz were ~ 3 times smaller than those for the disks.

The CaF_2 samples were immersed in pure liquid ^{3}He cooled by contact with the mixing chamber of a dilution refrigerator.[12] To avoid heating of the samples during the application of rf pulses, all of the components of the NMR tank circuit were thermally isolated from the sample, and mounted on a copper plate which was thermally anchored to the 1-K stage of the refrigerator.

A small amount of [DLX-6000 (Ref. 13)] fluorocarbon powder (18 mg) was included in the sample chamber. Comparison of the ^{19}F signal from the (rapidly relaxing) powder with that from the CaF_2 allowed calibration of the CaF_2 signal relative to its thermal equilibrium value at temperatures below 40 mK, when the CaF_2 equilibrium could not be reached in a reasonable time. The ^{19}F magnetization of the fluorocarbon powder obeys Curie's law and has a short, temperature-independent T_1.[10] Above 40 mK the CaF_2 equilibrium signal was used. The constant of proportionality relating the signal magnitude and inverse temperature was determined at high temperature where the temperature could be independently determined by measurement of the ^{3}He vapor pressure. Temperature could also be monitored and regulated by means of a resistor mounted on the mixing chamber. Uncertainties in temperature determination during a relaxation measurement had two sources: (i) Temperature regulation based on resistance measurements was made difficult at the lowest temperatures due to the extreme sensitivity of the resistor to electrical pickup. It was found that acceptably stable temperatures ($\pm 20\%$) could be achieved at these temperatures by allowing the refrigerator to run at a base temperature determined by ^{3}He circulation conditions. (ii) There was some difficulty in decomposing the observed ^{19}F signal into separate components due to the CaF_2 and that due to the fluorocarbon powder. Although the FID's from the two substances have substantially different time constants, the decomposition was made difficult by the usually much greater size of the CaF_2 signal. During the long time periods required for measurement of the relaxation times at low temperatures, this procedure was used to monitor the extent of temperature drift during the measurement. A rough temperature was determined before and after a measurement by saturating the CaF_2 signal and measuring the magnitude of the DLX signal alone shortly thereafter.

Two variable capacitors mounted inside the cryostat directly adjacent to the NMR coil could be adjusted by means of drive rods which extend to room temperature. This provided some capability of matching the transmission line impedance to that of the NMR coil. We measured relaxation rates at three ^{19}F Larmor frequencies: 6, 11.8, and 44 MHz, corresponding to $B = 0.15$, 0.295, and 1.1 T, respectively.

The relaxation rates span several decades, so we employed different techniques appropriate to the time scales involved. The magnetization was always destroyed initially, and its growth toward thermal equilibrium then monitored as a function of time. At high temperatures a saturate-τ-90° pulse sequence was used. At low temperatures where the relaxation times are long, up to tens of days, the recovering magnetization was measured periodically with small (1.5°) tipping pulses. The time dependence of this signal in conjunction with the thermal equilibrium value of the magnetization, M_{eq}, were used to find the relaxation rate. At temperatures above 40 mK, M_{eq} was measured directly. At very low temperatures the equilibrium magnetization could not be directly measured and so was inferred from the temperature as determined from the ^{19}F NMR signal from the DLX powder. At the lowest temperatures the magnetization could be followed for only $\sim 10\%$ of its recovery toward equilibrium, and we report T_1 values based on the initial slope and the independently measured or estimated equilibrium magnetization. At the higher temperatures (40 mK and above) the full curve of the recovery was followed. Within these limitations, the recovery seemed to be approximately exponential in all cases.

We employed a commercially available transceiver[14] to control rf pulses used to saturate and perturb the system and to receive the resulting signal. This signal was first amplified by a low noise broadband preamplifier before phase sensitive detection by the transceiver. The in-phase and quadrature outputs were digitized and magnitude of their vector sum integrated.

RESULTS AND DISCUSSION

Figure 1 summarizes the raw experimental data. At low field and high temperatures the T_1 values are in reasonable consonance with previous work: indeed our

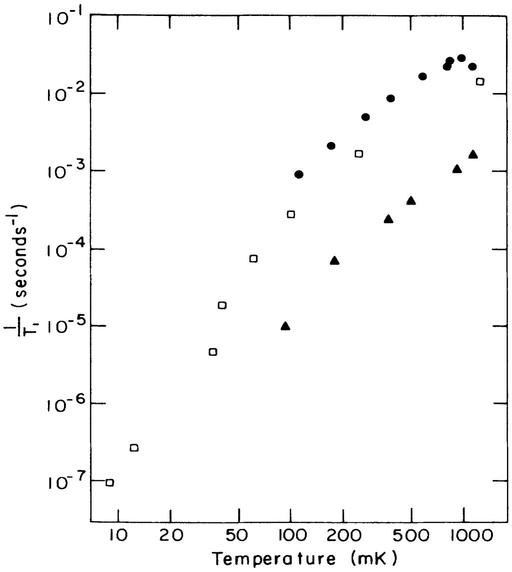

FIG. 1. Temperature dependence of the ^{19}F relaxation rate in CaF_2 disks. The rates were measured at ^{19}F Larmor frequencies of 6.0 MHz (filled circles), 11.8 MHz (open squares), and 44 MHz (filled triangles).

points at 6 MHz can be fit moderately well to a formula of the Beal-Hatton type, adjusting appropriately for the higher purity of our crystals. However, over a wider range such comparisons fail. Most significantly, as T is lowered T_1 increases *far* less rapidly than we anticipated. As a purely empirical fact, T_1 seems to be a function only of B_0/T, and indeed

$$\frac{1}{T_1} = 1.7\exp[-6.8(B/T)^{0.26\pm0.03}]\ \text{sec}^{-1} \qquad (2)$$

fits our data rather well, as shown in Fig. 2. We can give no physical interpretation to this formula.

It may be worthwhile discussing two possibilities that occurred to us in trying to rationalize the small values of T_1 observed at low temperatures: First, over the long time scales (hundreds of hours) of the experiments, very small sources of interference (laboratory vibrations, radio noise, transmitter leakage, etc.) may couple to the nuclear spins. However such sources are characterized by high or infinite effective temperatures and would therefore *saturate* the spins. In our measurements we observe the growth of magnetization from a saturated state toward an equilibrium value appropriate to a very low temperature. The lowest temperature at which we observe the complete recovery is ~40 mK, far below the temperature of any part of the surroundings except the ^{3}He bath itself.

Second, note that our crystals are always in contact with liquid ^{3}He, which as we know possesses nuclear moments and is capable of relaxing surface ^{19}F spins. Suppose the ^{3}He were actually to permeate the crystals, causing relaxation in some undefined way in the bulk. Quite a uniform distribution would be required: the requisite number, fineness and connectivity of cracks is hard to imagine. As for diffusion of He atoms through an intact crystal, any plausible estimate of the interatomic potentials involved[15] indicates an activation energy of at least several eV for this process.

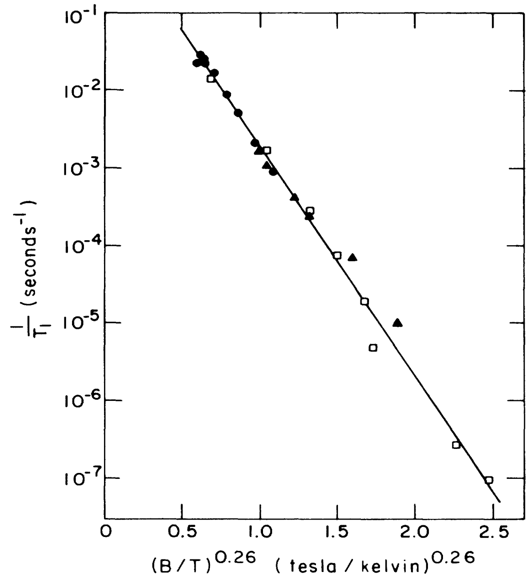

FIG. 2. ^{19}F relaxation rate at three Larmor frequencies: 6.0 MHz (filled circles), 11.8 MHz (open squares), and 44 MHz (filled triangles) plotted as a function of $(B/T)^{0.26}$.

While we have spoken only of CaF$_2$ in this paper, we have seen evidence of unexpectedly short T_1's in a number of other cases (protons in epoxy resins and solids such as gypsum, ^{19}F in coaxial cables, etc.). While we have made no systematic studies of these, the conclusion seems inescapable that there are unsuspected modes of nuclear relaxation at very low temperatures which deserve further study.

ACKNOWLEDGMENTS

We are most grateful to Dr. J. R. Norris of Argonne National Laboratory where the ESR spectrum of CaF$_2$ was obtained. We thank F. VanNice for assistance and J. R. Gaines for contributing to the initial planning of these experiments. One of us (O.G.) was supported by the Dr. Chaim Weizmann Foundation. This work was supported in part by the National Science Foundation.

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