First Direct Measurement of the Spin Diffusion Rate in a Homogenous Solid

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The first direct measurement of the rate of spin diffusion through a homogeneous sample is reported. The measurement was performed as an incoherent scattering experiment via a combination of pulsed gradient spin echo methods with multiple pulse, pulsed gradient spatial encoding. The measurement records the destruction of a spin magnetization grating by the random translation of spin magnetization associated with the flip-flop term of the homonuclear dipole-dipole interaction. For single crystal CaF_2, the measured parallel components of the spin diffusion rates are 7.1×10^{-12} cm^2/s along the [001] direction and 5.3×10^{-12} cm^2/s along the [111] direction, in good agreement with theoretical predictions. [S0031-9007(97)05199-5]

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Spin diffusion was one of the earliest concepts in NMR of solids having been put forth by Bloembergen in 1949 to account for the unexpectedly rapid spin lattice relaxation found in solids [1]. Since then it has been of considerable theoretical and experimental interest, and yet to date there has been no direct measurement of the spin diffusion rate in a homogeneous solid; we report the first such below.

The exploration of spin diffusion in a single crystal is appealing since the spin Hamiltonian is well known, the initial conditions are well defined, and the dynamics are kinematically simple. The homonuclear dipolar Hamiltonian contains the well-known "flip-flop" term, $I_+I_- + I_-I_+$, which permits energy conserving two-spin flips of antiparallel aligned spins, and these two-spin flips act as a means of transporting spin magnetization through the lattice. In Bloembergen's original analysis the transport is to relaxation sinks created by the fluctuating magnetic fields of paramagnetic impurities. The reduced bulk spin lattice relaxation time is then controlled by the spin diffusion mediated transport of magnetization to the sinks. A clear indication that spin diffusion does indeed govern the bulk relaxation rate is seen from the angular dependence of T_1 in cubic crystals [2,3]. In the absence of spin diffusion the T_1 of a cubic lattice is isotropic; the observed anisotropies arise from the angular dependence of the dipolar interaction on which the diffusion rate depends.

Over distance scales long compared to the few lattice spacings, the magnetization evolves according to a macroscopic diffusion equation. For the case of a sinusoidal magnetization grating, Redfield [4] connected the spin diffusion constant to the line shape moments. Of course, the short time behavior is unitary and a mark of the isolation of the spin system is that even over long times and for processes involving many spins, spin diffusion is reversible (by a sign change of an effective Hamiltonian), as shown by Waugh and co-workers [5]. In systems that may be described as a small cluster of spins, the unitary behavior is very pronounced [6,7], and the diffusion analogy is not applicable.

The archetype measurement of spin diffusion involves creating a nonuniform magnetization profile throughout the sample and then measuring its rate of return to spatial uniformity. The experimental challenges are (1) to create a spatially varying magnetization that has a characteristic length scale shorter than, or on the order of, the root mean square displacement during T_1 ($\Delta z_{\mathrm{rms}} = \sqrt{2DT_1}$ where $D \sim 10^{-12}$ cm^2/s), and (2) to create this profile over a volume that has a uniform spin Hamiltonian. Nearly all approaches to creating a spatially varying magnetization profile have involved the use of chemically heterogeneous samples, either based on the morphology of semicrystalline polymers [8], diffusion to defects [9], diffusion in blends [10,11], or exploring small spin systems [12]. While these measurements are useful to characterize the morphology of the sample, most have little relationship to theoretical studies since the spectral difference that permitted the creation of the magnetization profile complicates the analysis by introducing a spin diffusion bottleneck where the flip-flop term is no longer energy conserving. The case most widely explored in theoretical models is an oriented single crystal, such as CaF_2 [13–16].

Kuhns, Hammel, Gonen, and Waugh [17] attempted to carry out a direct measurement of spin diffusion in CaF_2 through a series of low temperature experiments of relaxation in a single crystal whose surface was efficiently relaxed through contact with a ^{3}He bath. The experiment was designed to measure the return to thermal equilibrium of a sample that was initially saturated, with special attention paid to the long time behavior so that surface effects would not be important. Unfortunately, the bulk ^{19}F relaxation time was unexpectedly fast preventing the long time scale necessary for the measurement.

We chose to approach a measurement of spin diffusion as an incoherent NMR scattering experiment. The essence of NMR scattering is to record the extent of microscopic transport of spin magnetization through a sample by directly observing amplitude and phase changes of a well defined spin magnetization grating. As is well known from coherent approaches to magnetic resonance imaging, the linear increasing rate of spin precession in a magnetic field gradient creates a spatial grating of the transverse nuclear spin magnetization. The grating is a spatially periodic modulation of the phase of the magnetization since over time each precessing spin picks up a phase factor of $\exp[-i\gamma(\partial B_z/\partial z)zt]$, where γ is the gyromagnetic ratio, and $\partial B_z/\partial z$ is the gradient strength. This grating is a linear ramp of the transverse magnetization's relative phase and the spatial period defines a wave number, k_0, that in the simplest case is proportional to the first moment of the gradient wave form. In an NMR scattering experiment such a magnetization grating is created, followed by an interval of evolution, and then the resultant changes in the grating are recorded. To date, NMR scattering measurements have relied on molecular diffusion to carry the spin magnetization through the sample; this is the first reported instance of a scattering measurement in a well defined sample where spin diffusion is responsible for the transport of spin magnetization. Fischer, Kimmich and Fatkullin [18] have recently observed a contribution to magnetization diffusion in polymer melts that is attributed to spin diffusion.

The displacement of the spin magnetization may be described by a displacement probability $P(\Delta z, t)$, so that the final grating is the convolution of the original linear phase ramp with $P(\Delta z, t)$,

$$\text{grating} = e^{ik_0 z} \otimes P(z,t) .$$

Since the NMR signal is the integral of the spin magnetization over the sample (or the spatially invariant portion of the grating), to measure the amplitude and phase of the k_0 component of the grating, a second interval of spin precession in the magnetic field gradient is required to unwind the grating. The NMR signal is thus a direct measurement of a selected Fourier component of the displacement probability,

$$\text{signal} = \int P(z,t) e^{-ik_0 z} dz .$$

The overall measurement is outlined in Fig. 1(a). In the long-time–many-spin limit of spin diffusion we expect to observe a Gaussian displacement probability, and therefore the magnetization grating is blurred by the random motion of the spin magnetization, $M_z(z,\Delta) = M_0 e^{-ik_0 z} \otimes 1/\sqrt{2\pi\sigma}\, e^{-z^2/2\sigma^2} = M_0 e^{-ik_0 z} e^{-k_0^2 D\Delta}$, where $\sigma = \sqrt{2D\Delta}$, and the grating is attenuated by $e^{-k_0^2 D\Delta}$. Therefore the rate of signal attenuation with spin diffusion time Δ provides a direct measurement of the spin diffusion constant D.

In the case of a solid sample with strong homonuclear dipolar couplings, the measurement must be carried out in such a fashion as to account for both the short spin-spin relaxation time, and to suspend spin diffusion during the preparation of the magnetization grating. A similar requirement is encountered in solid state imaging [19] where a combination of multiple pulse coherent averaging interspersed with pulsed magnetic field gradients [20]

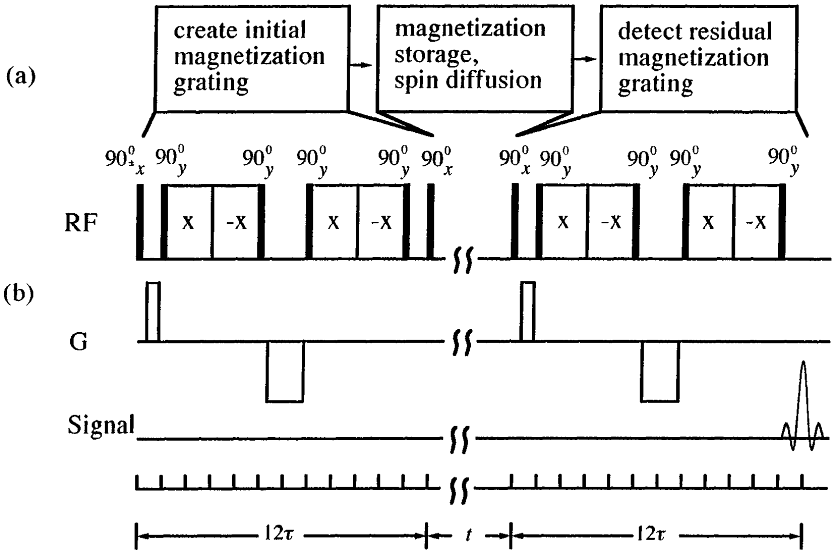

FIG. 1. Schematic (a) and detailed diagram (b) of the NMR incoherent scattering measurement used to measure the rate of spin diffusion in a homogeneous solid. The method starts by creating a magnetization grating through the otherwise uniform sample. This grating results from the differential rates of spin precession for spins at different spatial offsets in a linear magnetic field gradient. As shown in (b), the time available to create the grating is lengthened by a pair of magic echo sequences which have the added advantage of simultaneously interrupting spin diffusion. During the storage time the z component of the grating is slowly blurred (or attenuated) by spin diffusion while the transverse components rapidly decay due to the short spin-spin relaxation time. The final period removes the spatial variation in the phase so that the extent of attenuation may be measured, and again during this period spin diffusion is interrupted. To measure the spin diffusion constant a series of such experiments was carried out varying both the pitch of the grating and the diffusion (or storage) time.

TABLE I. Details of the experimental gradient conditions and resultant gratings that were used for the measurements show in Fig. 2.

	Gradient pulse length (μs)	Average current (A)	Average gradient strength (G/m)	$k/2\pi$ (cm^{-1})
[001] o	110	198.3	13 300	5 900
[001] x	90	207.4	13 900	5 000
[001] *	70	217.4	14 600	4 100
[111] o	200	183.9	12 300	9 900
[111] +	180	175.8	11 800	8 500
[111] x	140	186.3	12 500	7 000
[111] *	110	203.7	13 600	6 000

has been employed to interrupt the dipolar evolution during the creation of magnetization gratings. In this experiment a magic echo sequence is used to periodically refocus the evolution from dipolar coupling and since spin diffusion is also driven by dipolar coupling there is no net spin diffusion during the creation of the grating. The experimental ability to suppress spin diffusion during the creation of the grating makes the analysis of the diffusion data very simple and is analogous to being in the "delta gradient pulse" limit for pulsed gradient diffusion measurements in liquids.

The detailed pulse sequence for the experiment is diagramed in Fig. 1(b) and described in the figure caption. Some details of the gradient strengths and gradient pulse lengths are provided in Table I. The observed signal is attenuated by both spin diffusion and spin lattice relaxation, according to $e^{-k^2 D_{\|} t} e^{-t/T_1}$, where $D_{\|}$ is the spin diffusion coefficient for diffusion along the direction of the main magnetic field.

Figure 2 shows the results of a series of such measurements where the time over which spin diffusion occurred was systematically varied from 10 to 60 s for crystal orientations of [001] and [111], and the length scales of the magnetization grating were about 1 to 3 μm. The contribution from the T_1 was measured in a separate set of experiments at these orientations and has been subtracted. These two orientations were chosen since they show the greatest variation in ^{19}F line shape second moments [21] (see inset of Fig. 2). As expected, spin diffusion is Gaussian over this length scale and changes with orientation. The results are compiled in Table II along with a theoretical prediction of Redfield and Yu from a moment calculation [14] (the value for each orientation was calculated for a 200 × 200 × 200 lattice), Borckmans and Walgraef based on irreversible statistical methanics [15], and a classical spin dynamic approach of Tang and Waugh [16].

The accuracy of the measured spin diffusion coefficients depends on the calibration of the gradient coil constant, the gradient wave form, an accurate measurement of T_1, and the correct orientation of the crystal. A detailed description of the experimental design and probe geometry will be reported elsewhere, here we will focus on estimating the errors. The gradient coil constant was calibrated to the known diffusion constant of water at 15 °C and is 67 ± 2 G/cm A. The gradient wave form was directly measured by digitizing the voltage over a shunt to avoid introducing calibration errors for the gradient coil heating. Any errors in gradient calibration are systematic and appear in the absolute diffusion constant, but not in the ratio of the diffusion constants at the two orientations. The T_1 was measured via the same sequence without a magnetization grating. The sample was oriented and cut with the help of x-ray diffraction techniques, but the small (<0.8 mm) sized crystals and limited gradient volume made handling difficult. The free induction decays

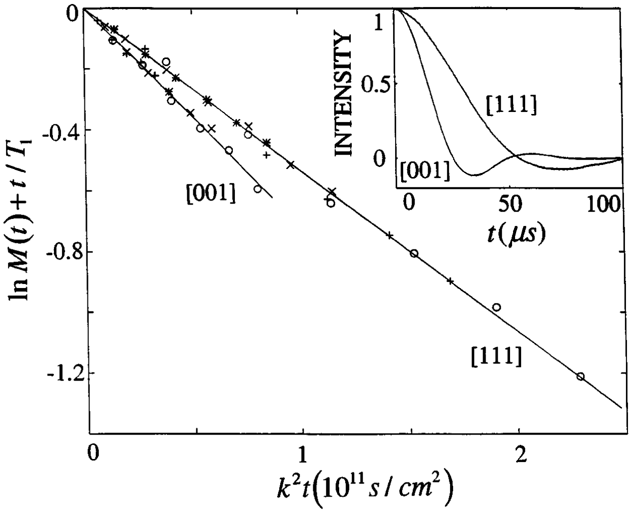

FIG. 2. Measured signal attenuation from a CaF_2 single crystal oriented with either the [001] or [111] axis along the main magnetic field. The contributions to the signal attenuation from T_1 relaxation have been subtracted. The diffusion measurements were made with the sequence shown in Fig. 1, with $\tau = 60$ μs for the [001] orientation and $\tau = 60$ or 100 μs for the [111] orientation. Both the gradient pulse lengths and the gradient strengths were varied in the experiments; the details are contained in Table I. Notice that for each orientation the data are well described by a straight line, and that the [001] data decay more rapidly than does the [111]. The inset shows the free induction decay for the two orientations.

TABLE II. Compiled results of this measurement and previous predictions for single crystal CaF_2. T_1 is the spin-lattice relaxation time, and $D_\parallel$ is the component of spin diffusion coefficient parallel to the external magnetic field.

Orientation	[001]	[111]
T_1 (s) (measured)	114.7 ± 5.3	156.8 ± 9.7
$D_\parallel$ (10^{-12} cm^2/s) (measured)	7.14 ± 0.52	5.31 ± 0.34
$D_\parallel$ (10^{-12} cm^2/s) (Ref. [14])	8.22	6.71
$D_\parallel$ (10^{-12} cm^2/s) (Ref. [15])	6.98	4.98
$D_\parallel$ (10^{-12} cm^2/s) (Ref. [16])	7.42	⋯

shown as the inset of Fig. 2 are, however, consistent with those previously reported and so any errors in crystal orientation are small.

The agreement between the measured values and theoretical predictions are quite good; in addition, the ratio of the diffusion constants $D_\parallel(0,0,1)/D_\parallel(1,1,1) = 1.3$, which does not suffer from a systematic error from the gradient coil constant calibration, agrees well with the predictions of 1.2 [14] and 1.4 [15].

The spin diffusion rate was also measured for a second crystal with a shorter T_1, therefore containing more defects, oriented along the [111] direction. As expected, the measured $D_\parallel$ is not a function of the defect density. In these scattering measurements the defects introduce spectral mismatches in the surrounding spins, and hence, locally suppresses the spin diffusion rate. The flow of magnetization which attenuates the grating, therefore naturally goes around the defect and excludes it from the dynamics. Provided that the defect density is sufficiently low, the effective tortuosity so introduced does not measurably increase the diffusion constant.

In conclusion, we have made the first direct measurement of spin diffusion rate in a homogeneous solid, single crystal CaF_2, and the absolute value and orientation dependence agree well with theoretical predictions. The experiment is an example of an incoherent NMR scattering measurement with multiple pulse coherent averaging to both lengthen the time during which a grating may be established and interrupt spin diffusion during the creation of the grating. The measurement required a special purpose NMR probe with 20 000 G/cm pulsed gradients, to be described in detail elsewhere. Using the framework of NMR scattering and our newly developed apparatus, it will be possible to extend these studies to the investigation of spin dynamics in a strongly coupled system as a function of both time and length scales. We anticipate that such studies will provide information that was previously unmeasurable on multibody dynamics in the mesoscopic domain.

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