

## Power-Law Relaxation of Spin- $\frac{1}{2}$ Nuclei in Solids \*

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We are using  $^{29}\text{Si}$  NMR spectroscopy to characterize the chemical structure of a variety of silicate materials (1, 2). Since these studies usually require the recording of quantitative spectra, a direct polarization experiment with magic angle spinning (MAS) is employed. We have found that many samples do not possess a well-defined  $T_1$ , but rather exhibit a power-law relationship between the magnetization intensity and pulse delay time. This behavior is the result of relaxation of spin- $\frac{1}{2}$  nuclei by paramagnetic impurities under MAS conditions (3). This Note describes the complications one must consider when spectra of spin- $\frac{1}{2}$  nuclei in solids are recorded, how the relaxation by paramagnetic impurities may be used to characterize the spatial structure of a material, and some proposals by which the very long recovery times of these materials can be circumvented.

Figure 1 shows the magnetization recovery for an  $\alpha$ -quartz powder from Alfa Products recorded at 4.7 T using a comb saturation sequence, direct polarization, and MAS at 4 kHz. The solid line is a theoretical fit assuming a 37 s exponential recovery of the magnetization. The fit is reasonable and considering the effort needed to acquire additional data (3600 scans recorded at 10 s and 360 scans recorded at 100 s), one is tempted to conclude that the 100 s pulse delay is adequate for a reasonably quantitative spectrum. This conclusion would lead to serious error.

Figure 2 shows the magnetization recovery for the same  $\alpha$ -quartz sample for much longer delay times. The recovery is plotted on a log-log scale from which it is obvious that the magnetization follows power-law behavior over five decades of time. Calibration of the spectrometer with silicate samples having shorter relaxation times confirms that the magnetization is near equilibrium for the longest times recorded in Fig. 2. Spectra recorded at 100 s would have accounted for only 2% of the equilibrium magnetization and the relative intensities of a multicomponent spectrum could have suffered serious distortion.

When recording the spectra of samples which exhibit exponential recovery, one can predict the equilibrium magnetization on the basis of experiments employing delay times

on the order of  $T_1$ . Note that there is no such analogy when the sample exhibits power-law behavior. The data for delay times ranging from 1 to 100,000 s give no indication of the equilibrium magnetization. For this reason, we routinely calibrate the response of the spectrometer so that if the spin density and mass of the sample are known, we can predict when the recorded magnetization is approaching equilibrium.

Power-law behavior of the magnetization recovery has been observed previously for paramagnetically doped sol-gel-derived silicate samples (3). Power-law behavior for spin- $\frac{1}{2}$  nuclei is expected whenever the sample is undergoing MAS and its relaxation is dominated by randomly distributed paramagnetic impurities. Although the samples in this study were not intentionally doped, they contain low levels of paramagnetic impurities (4). The power-law exponent of 0.54 is reasonably close to the value of 0.50 predicted for a three-dimensional material.

Figure 3 shows the magnetization recovery of an  $\alpha$ -quartz sample which has been subjected to a 22 GPa shock wave (5). The recovery again displays power-law characteristics. However, the power-law exponent of the shocked sample is only 0.39. Representative spectra for the unshocked and shocked quartz samples are shown in Fig. 4. The spectra for the unshocked sample have qualitatively similar features, independent of recovery time. The spectra for the shocked sample appear quite different for short and long recovery times. For short recovery times, the spectra of the shocked sample exhibit both broad and narrow components. The narrow component corresponds to the normal crystalline phase as observed for the unshocked sample, while the broad component corresponds to a disordered phase produced by the shock wave. For short recovery times, the broad component dominates, while for long recovery times, the narrow component dominates to the extent that the contribution of the broad component is not observed. These spectra illustrate the importance of recognizing the relaxation characteristics of a complex material. By analyzing the spectra of the shocked quartz, we are able to estimate the proportion of disordered to ordered phase and determine the fractal dimension of each phase (6).

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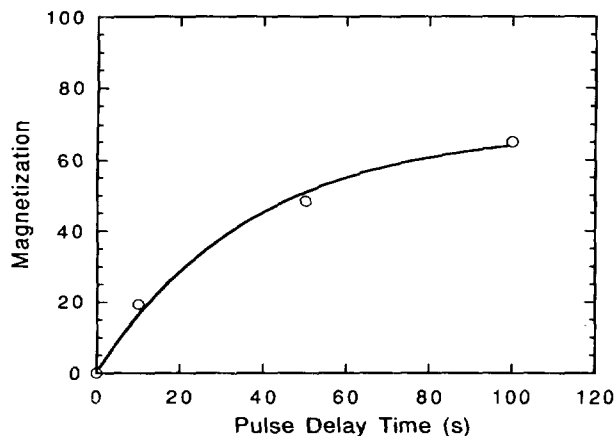


FIG. 1. The magnetization recovery of an  $\alpha$ -quartz sample for times up to 100 s. The solid line is a theoretical fit assuming a 37.2 s exponential recovery.  $M = M_0[1 - \exp(-t/T_1)]$ .

The spectra for both the unshocked and the shocked samples take a very long time to accumulate. We have considered methods by which this time can be reduced. Figure 5 shows the magnetization recovery versus pulse delay time of unshocked quartz samples with and without MAS. The recovery curve for the sample without MAS was obtained by allowing the sample to polarize while static and then applying MAS during the observation period. By eliminating MAS, nuclear spin diffusion is again effective and the relaxation rate increases dramatically. The magnetization recovery of the static sample is described reasonably well by a spin-lattice relaxation time of 3800 s. More importantly, the time to acquire a quantitatively correct spectrum is reduced an order of magnitude by application of this simple nonspin/spin sequence.

Figure 6 shows the relaxation time of the magnetization for the unshocked sample in zero field. These measurements

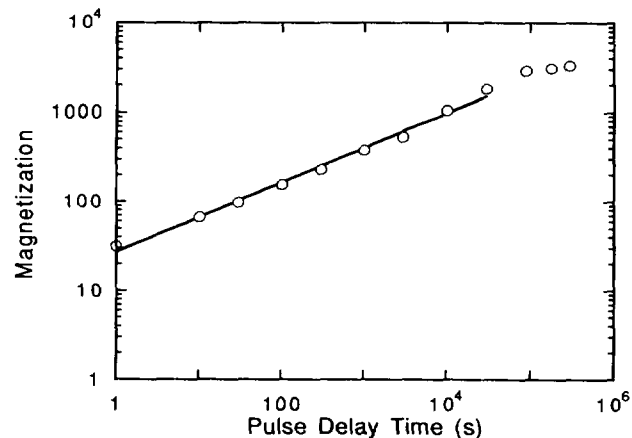


FIG. 3. The magnetization recovery of an  $\alpha$ -quartz sample subjected to a 22 GPa shock wave. A power-law fit is shown, although the magnetization consists of components with differing relaxation behavior (see Fig. 4 and text).  $M = At^a$ ,  $a = 0.39$ .

were obtained by allowing the spins to polarize, removing the spins from the magnetic field for various periods of time, and then restoring the magnetic field and sampling their po-

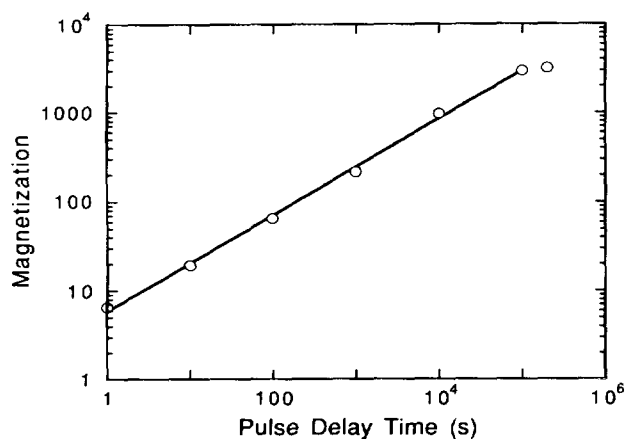


FIG. 2. The magnetization recovery of an  $\alpha$ -quartz sample on a log-log scale. The recovery follows power-law behavior over five decades of time.  $M = At^a$ ,  $a = 0.54$ .

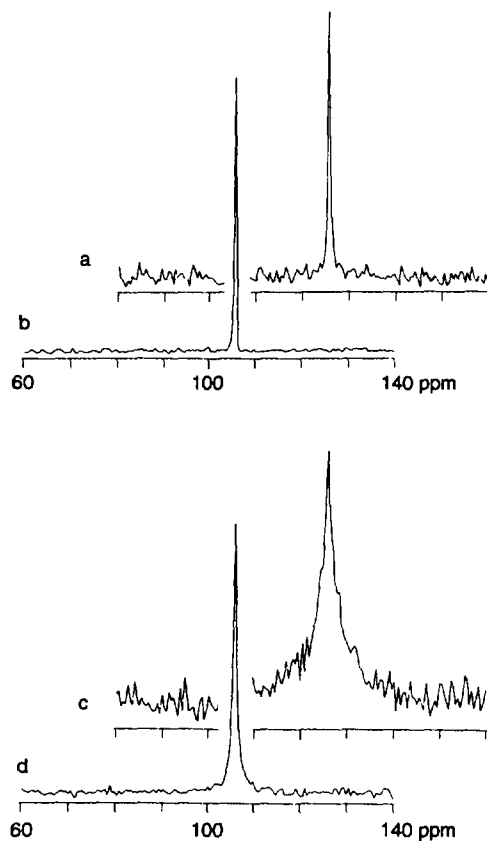


FIG. 4. Representative spectra of the unshocked  $\alpha$ -quartz sample at (a) 10 s and (b) 100,000 s recovery times and of the shocked  $\alpha$ -quartz sample at (c) 10 s and (d) 90,000 s recovery times.

larization. This adiabatic demagnetization/magnetization has been described previously (7). The relaxation time in zero field is approximately 130 s. This result suggests that one could simultaneously polarize several samples in a region of the magnet adjoining the probe or in a nearby magnet and then transport them to the probe for observation under MAS conditions.

MAS can quench the spin diffusion of dilute spin- $\frac{1}{2}$  nuclei in solids, thereby increasing the relaxation time and changing the functional form of the magnetization recovery. Recognition of this phenomenon is important when recording quantitative spectra and also suggests operational procedures by which the long times to record spectra of these materials may be reduced.

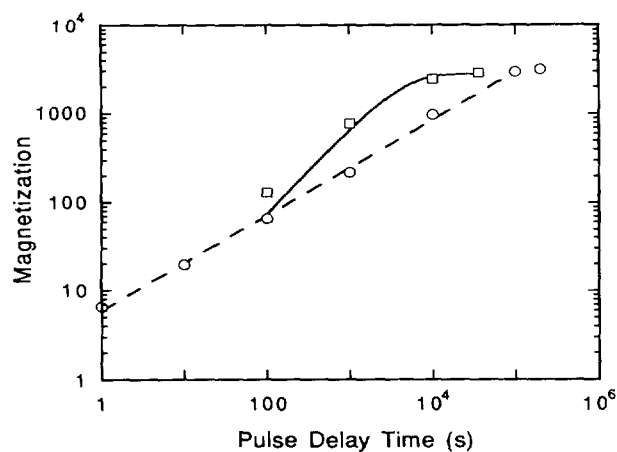


FIG. 5. The magnetization recovery of a static (—)  $\alpha$ -quartz sample compared to that of the same sample undergoing MAS (---). The recoveries were fitted by exponential and power-law functions respectively.  $M = M_0[1 - \exp(-t/T_1)]$ .  $T_1 = 3800$  s.

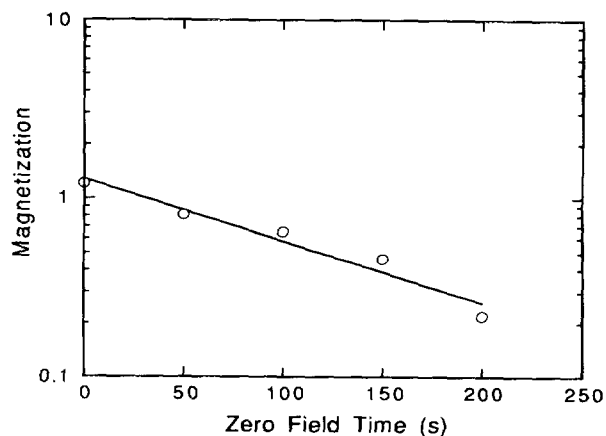


FIG. 6. The zero-field magnetization decay of an  $\alpha$ -quartz sample.  $M = M_0 \exp(-t/T_1)$ .  $T_1 = 380$  s.

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