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High-field QCPMG NMR of strontium nuclei in natural minerals

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Abstract

The only stable NMR-active isotope of strontium, ^{87}Sr, is a spin-9/2 quadrupolar nucleus that has a low gyromagnetic ratio, a low natural abundance, and a large nuclear electric quadrupole moment. In this work, we utilize the quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) pulse sequence and a 21.14 T NMR spectrometer at the Pacific Northwest National Laboratory to characterize the strontium sites in the natural minerals strontianite ($SrCO_3$) and celestine ($SrSO_4$). QCPMG at 21.14 T was found to provide sensitivity enhancements of roughly two orders of magnitude over Hahn-echo experiments at an 11.74 T magnetic field. We extracted the quadrupolar parameters for the strontium nuclei through iterative simulations of the experimental spectra with the SIMPSON program by Bak, Rasmussen, and Nielsen. The data show that the quadrupolar parameters of ^{87}Sr appear to be highly sensitive to the symmetry of the strontium coordination environment and can thus provide information about the strontium binding environment in complex systems.

Keywords: Strontium; QCPMG; Quadrupolar coupling constant; Asymmetry; Strontianite; Celestine; Natural minerals; High-field solid-state NMR

1. Introduction

A majority of the NMR-active nuclei in the periodic table (including ^{87}Sr, the only stable NMR-active isotope of strontium) are quadrupolar, meaning they have a non-zero nuclear electric quadrupole moment (eQ). Most of the nuclei in the periodic table are therefore susceptible to the quadrupolar interaction, which occurs when the electric quadrupole moment of a nucleus interacts with an electric field gradient at the nucleus, effectively shifting the magnetic spin substates. The quadrupolar interaction is one of the most variable internal NMR interactions, ranging from non-existent to tens of MHz in interaction strength, and thus can be highly sensitive to variations in structure. However, if the magnitude of the quadrupolar interaction is large, the resulting NMR resonances can be very broad, resulting in limited sensitivity. Strontium-87 is known to possess a large nuclear electric quadrupole moment (0.36×10^{-28} m^2 compared to 0.12×10^{-28} m^2 for ^{23}Na) and therefore develops broad resonances in the presence of any appreciable electric field gradient [1,2]. Solid-state ^{87}Sr NMR is plagued by other intrinsic properties of the ^{87}Sr nucleus as well, namely a low natural abundance (~7%) and a low gyromagnetic ratio ($\gamma = -1.163 \times 10^7$ T^{-1} s^{-1}); factors that imply low sensitivity and complications from acoustic probe ringing. As a direct result of these properties, very few reports containing solid-state ^{87}Sr NMR spectra appear in the literature [1–5]. It is therefore necessary to employ sensitivity enhancing NMR methods to perform routine NMR analyses of strontium in crystalline and more complex systems in a time effective fashion.

Despite the availability of techniques for overcoming sensitivity limitations of low-γ quadrupolar nuclei, in only two cases are sensitivity enhancing NMR methods applied to ^{87}Sr [2,5]. The majority of the literature regarding solid-state ^{87}Sr NMR consists of studies with strontium nuclei in highly symmetric environments [3–5]. In lattice locations with tetrahedral, octahedral, or cubic symmetry, the electric field gradient is theoretically zero and therefore no significant quadrupolar interaction is present. Weber

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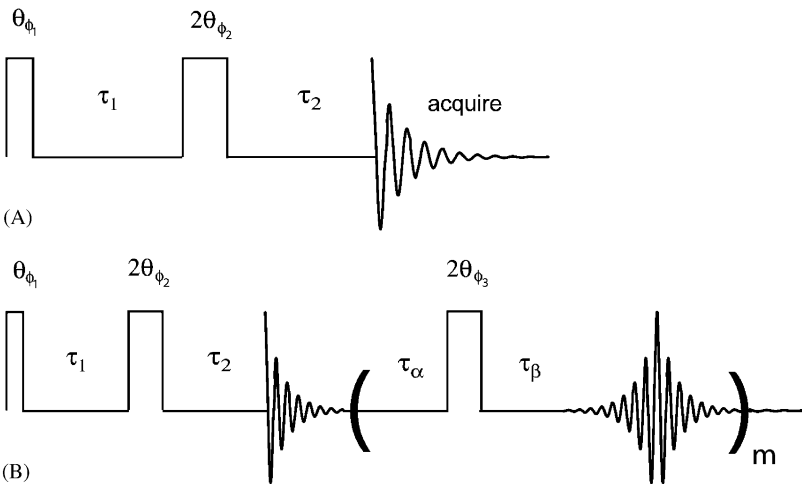

Fig. 1. Pulse sequence schematics for (A) Hahn-echo and (B) QCPMG experiments.

and Allen studied the changes in strontium quadrupolar parameters in strontium titanate (cubic symmetry around the strontium nuclei) as the material went through a phase change at 110 K [3]. A recent paper in which Gervais et al. examined mixed barium–strontium titanates at various barium to strontium ratios presented preliminary ^{87}Sr NMR data showing that the narrow strontium titanate resonance became broader with increasing barium content until they could no longer detect a strontium signal with Hahn-echo methods [4]. We recently published a study where we demonstrated the merit of MAS NMR methods for studying strontium in highly symmetric environments and used the results to interrogate the distribution of electric field gradients about ^{87}Sr nuclei due to defects in the crystal structures of SrO, $SrCl_2$, and SrF_2 [5]. The remaining two publications to date contain solid-state ^{87}Sr spectra in systems where a moderate electric field gradient is present. Bastow published a study examining the electric field gradient at the cation site in alkaline earth carbonates with static Hahn-echo methods in which he reports the ^{87}Sr spectrum and quadrupolar parameters of strontium carbonate [1]. Larsen et al. have produced the only publication to date where a sensitivity enhancing NMR pulse sequence is applied to ^{87}Sr nuclei [2]. They extracted the quadrupolar and chemical shift parameters of ^{87}Sr in $Sr(NO_3)_2$ and $SrMoO_4$ from spectra acquired with the quadrupolar Carr–Purcell–Meiboom–Gill (QCPMG) pulse sequence at 14.09 T ($\nu_0^{1H} = 600$ MHz).

The QCPMG experiment used by Larsen et al. is one of the most promising methods for the general examination of low-γ quadrupolar nuclei with solid-state NMR. A number of authors have shown that the QCPMG sequence provides up to an order of magnitude sensitivity enhancement over conventional echos (at constant field strength) for low-γ quadrupolar nuclei [2,6–8]. During a QCPMG experiment, a $\theta-2\theta$ echo sequence and half-echo acquisition is followed by a series of 2θ pulses with a full-echo acquisition after each 2θ pulse (Fig. 1) [9]. The Fourier transform of the resulting NMR signal is a series of sharp peaks that map out the static powder pattern, providing gains in sensitivity without sacrificing the information that is contained in the powder pattern. The frequency separation of the peaks corresponds to the inverse of the time interval between echo maxima in the NMR signal and is thus readily controllable, although subject to system-dependent relaxation rates and instrumental sampling limitations. QCPMG NMR provides an additional advantage in that the sensitivity of the experiment increases by a factor of $\sqrt{2n}$ due to the acquisition of n full echos (rather than half-echos) over the course of the n echo loops. Additionally, many data processing methods exist that further improve the sensitivity of QCPMG experiments [8], as described in detail by Lefort [10]. For these reasons, QCPMG NMR has been applied at a variety of field strengths to examine nuclei that have traditionally been difficult to study with solid-state NMR. Larsen and colleagues have used QCPMG techniques to study ^{67}Zn in metalloproteins, organic, and inorganic compounds as well as ^{39}K, ^{25}Mg, ^{87}Rb, and ^{87}Sr in inorganic salts [2,11,12]. QCPMG experiments have also been used to study ^{25}Mg in organic compounds [8,13], ^{91}Zr in organic compounds [14], and ^{35}Cl and ^{37}Cl in organic hydrochloride salts [15].

One motivation for improving the sensitivity of ^{87}Sr NMR methods is to use solid-state NMR to learn about the interactions of strontium cations sorbed by clay minerals and zeolites. Knowledge of these interactions will contribute toward an understanding of strontium sequestration and transport when caustic nuclear waste solutions are released into the environment, such as during failures in the integrity of waste storage tanks at the United States Department of Energy Hanford site in Richland, Washington. The achievement of this goal requires (i) successful application and evaluation of existing sensitivity enhancing NMR methods to ^{87}Sr, (ii) studies of strontium environments in simple systems, and (iii) applying lessons from (i) and (ii) to study strontium in strontium-saturated clay minerals and zeolites. In this study, we take advantage of the stable 21.14 T magnetic field available at the Pacific