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# Spatially Resolved Spectroscopy and Structurally Encoded Imaging by Magnetic Resonance Force Microscopy of Quadrupolar Spin Systems

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In 1991 a new method for detecting nuclear magnetic resonance (NMR) signals was suggested by Sidles.[1] The method, called magnetic resonance force microscopy (MRFM), is based on mechanical detection using an AFM-type cantilever as depicted in Figure 1. The principle is based on the fact that if a sample carrying a magnetic dipole moment is put on the cantilever a force $F_z = M_z \cdot \partial B / \partial z$ is exerted on this lever in the presence of a magnetic field gradient.

The magnetization, and therefore the force, is made time dependent by inverting the magnetization adiabatically. This is achieved by sweeping the RF frequency through resonance for a particular spin species. This process is repeated in step with the cantilever eigenfrequency. The resulting oscillatory deflection is observed in the MRFM experiment. The method has been under development in an attempt to overcome the inherent insensitivity of inductive NMR aimed at reaching a sensitivity allowing the detection of a single spin.[2]

In this report, we show the first MRFM results for quadrupolar nuclei. As will be demonstrated, this holds great promise for the study of materials. Quadrupolar nuclei enable us to perform localized spectroscopy in the rotating frame using the nutation NMR experiment. The use of strong magnetic field gradients allows measurements in a spatially resolved manner with $\mu$m resolution, additionally a structural contrast can be added. Although adiabatic passages in quadrupolar spin systems are more involved compared to spin $^1/_2$ systems,[3] the method can still be applied for modulating $I_z$ and getting a mechanical response. We demonstrate the method for different compounds and nuclei with different spin numbers, i.e., $^{23}$Na, $^{69}$Ga, $^{71}$Ga ($I = {}^3/_2$), $^{27}$Al ($I = {}^5/_2$), and $^{51}$V ($I = {}^7/_2$). The MRFM setup used is the basic sample-on-cantilever design with a laser interferometer according to Rugar et al.[2] This design has been augmented with a digital waveform generator to enhance the radio frequency (RF) control to seamlessly mix continuous wave and pulsed RF generation.[4] All measurements have been performed at room temperature by using a 4.2 T superconducting magnet and an iron gradient source generating a field gradient of up to ~1000 T/m at the sample position.

Various groups[4−6] have realized the observation of $^1$H nuclei in inorganic salts, such as $(NH_4)_2SO_4$, under ambient pressures and temperatures. At ambient pressure the quality factor $Q$ of our cantilever was about 100, insufficient for the observation of nuclei other than protons. Evacuating the probehead to a pressure of the order of $10^{-6}$ mbar increased the cantilever $Q$ to ~12 000, allowing the observation of $^{23}$Na nuclei in a 2 $\mu$m slice of a ~$20 \times 20 \times 10$ $\mu$m$^3$ NaCl crystallite using only two scans. NaCl forms a perfectly cubic crystal and therefore the $^{23}$Na nucleus does not experience large anisotropic interactions and has favorable relaxation parameters ($T_1 \sim 10$ s, $T_{1\rho} \sim 3$ s) for MRFM detection. To investigate possible applications of the method in realistic materials science we explored the possibility of observing $^{69}$Ga, $^{71}$Ga, and $^{27}$Al in device type GaAs and AlGaAs layers. As shown in Figure 2, observation of these nuclei proved feasible in 1 $\mu$m layers despite the far less favorable relaxation parameters ($T_1 \sim 0.2$ s, $T_{1\rho} \sim 0.07$ s). Even more demanding is the observation of $^{51}$V in polycrystalline $V_2O_5$, which is of interest in catalysis. Considering the small average crystallite size of $<1$ $\mu$m$^3$ an ensemble of crystals was glued together to give a sample of ~$20 \times 20 \times 10$ $\mu$m$^3$. Even with a $T_{1\rho}$ as short as 35 ms a reliable signal was obtained.

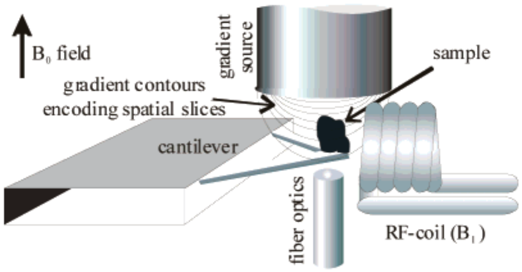

***Figure 1.*** Schematic display of a probehead for performing magnetic resonance force microscopy. The magnetic field gradient causes a spatial NMR frequency encoding that can be exploited for imaging purposes by means of varying either the gradient position or the RF irradiation frequency. The sample slice nuclear magnetization is periodically inverted by application of repetitive fast adiabatic passages. Combined with the static field gradient this causes modulation of the force acting on the sample. This modulating force is detected by using an AFM cantilever of which the deflection is monitored by means of a laser interferometer.

Quadrupolar nuclei serve as probes for their local environment, i.e., via the quadrupolar coupling one can derive structural information about the lattice. For instance, a nucleus in a cubic lattice experiences no external electric field gradient and will therefore exhibit no quadrupolar coupling. On the other hand, lattice sites experiencing an asymmetric local charge distribution are subject to large quadrupolar interactions. One of the methods for studying the quadrupolar interaction in regular solid-state NMR is nutation spectroscopy introduced by Samoson and Lippmaa.[7] In nutation NMR the evolution of the spin system is studied in the rotating frame during RF irradiation.

This evolution is monitored by recording the modulation of the NMR response as a function of the RF pulse length $\tau_p$. The nutation response is very sensitive to the ratio of the quadrupole frequency $\omega_Q$ and the RF field strength $\omega_1$. In the limiting case that $\omega_Q \sim 0$ the signal is modulated with $\sin(\omega_1 \tau_p)$. In the case of $\omega_Q \gg \omega_1$ the modulation frequency amounts to $(I + {}^1/_2)\omega_1$. In intermediate cases all odd-order transition frequencies will be present in the nutation spectrum of a single crystallite.[8] The nutation technique, affecting

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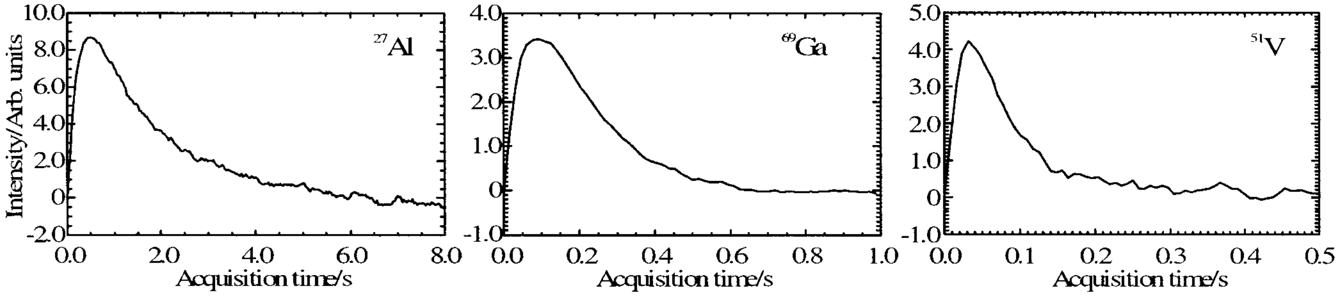

***Figure 2.*** MRFM signals obtained from various compounds showing the feasibility of obtaining reliable results from several quadrupolar nuclei by means of MRFM. From left to right: $^{27}$Al in a crystal AlGaAs ($I = {}^5/_2$), $^{69}$Ga in a single-crystal GaAs ($I = {}^3/_2$), and $^{51}$V in $V_2O_5$ powder ($I = {}^7/_2$).

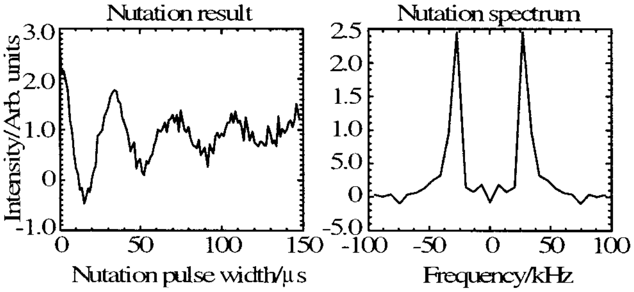

***Figure 3.*** Integrated signal intensity of an MRFM experiment following an on-resonance RF nutation pulse of variable width (left) and corresponding Fourier transform showing the nutation spectrum (right). The detected sample slice is ~4 × 25 × 35 $\mu$m.

single or multiple transitions depending on $\omega_Q/\omega_1$, can be incorporated in MRFM experiments by monitoring the mechanical signal amplitude as a result of the modulation of the $I_z$ operator after an on-resonance RF pulse. An advantageous feature of nutation NMR is that it is not affected by the presence of the large field gradient other than introducing offset effects. The possibility of performing spatially localized nutation spectroscopy is shown in Figure 3 for $^{69}$Ga in a ~4 $\mu$m GaAs layer. Clearly the signal modulation consists of a single well-defined frequency, in this case identical with the RF field strength $\omega_1$ as expected for the cubic GaAs structure. The damping of the signal is due to RF inhomogeneity and offset effects over the excitation slice.

The different response of quadrupolar nuclei to an on-resonance pulse depends on the quadrupolar interaction and can therefore be exploited for imaging of materials with a contrast function depending on the local structure experienced by the nuclei. A pulse acting as a $\pi/2$-pulse on spins in a cubic environment ($\omega_Q = 0$) will be felt as a $\pi$-pulse by spins in a very distorted environment ($\omega_Q \gg \omega_1$). Applying such a “quadrupolar filter” in an imaging experiment allows one to enhance or suppress signals of nuclei in a specific position in the overall image. This is demonstrated in Figure 4, showing the 1D image of a NaCl particle on top of a $Na_2C_2O_4$ crystallite.

As NaCl has a cubic structure $^{23}$Na does not experience a quadrupolar interaction, whereas in sodium oxalate the quadrupolar interaction is very large ($C_{qcc} = 2.5$ MHz, $\eta = 0.74$). The left image is the regular MRFM image reflecting the $^{23}$Na spin density with a 11 $\mu$m resolution. In the right image a quadrupolar filter was applied prior to the imaging experiment allowing one to practically eradicate the signal from the cubically symmetric NaCl particle from the image; the contrast of the oxalate is only slightly affected due to offset effects during the nutation filter pulse.

The ultimate goal of MRFM is to produce atomic-resolution images of molecular structures, e.g., to visualize active sites on catalyst surfaces, defects in solids, dopants in semiconductors, or binding sites in viruses. This imaging should be possible in situ in a nondestructive way. The present contribution is an important step on this road. In relevant materials amenable to studies by MRFM half-integer quadrupolar nuclei are abundant. We demonstrated that it is possible to perform spatially localized spectroscopy enabling one to superimpose a contrast function depending on the local lattice structure onto images. In this respect imaging with true chemical specificity has been achieved. In combination with future sensitivity enhancements and an inverted design of the apparatus with the gradient source on the cantilever this should provide a very powerful scanning probe technique.

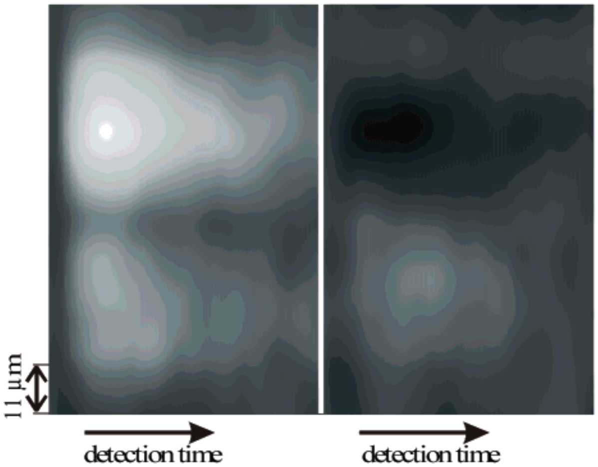

***Figure 4.*** 1D image of a crystallite of NaCl on top of a crystallite of $Na_2C_2O_4$ obtained by stepping the RF frequency. The left image shows the spin densities in the particles. The right image shows the same spatial region but now a contrast filter is applied, based on the local quadrupole interaction, that selectively cancels regions with $C_{qcc} = 0$.

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## References

(1) Sidles, J. A. *Appl. Phys. Lett.* **1991**, *58*, 2854.
(2) Rugar, D.; Yannoni, C. S.; Sidles, J. A. *Nature* **1992**, *360*, 563.
(3) Veenendaal, E. v.; Meier, B. H.; Kentgens, A. P. M. *Mol. Phys.* **1998**, *93*, 195.
(4) Verhagen, R.; Hilbers, C. W.; Kentgens, A. P. M.; Lenci, L.; Groeneveld, R.; Wittlin, A.; van Kempen, H. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4025.
(5) Rugar, D.; Züger, O.; Hoen, S. T.; Yannoni, C. S.; Vieth, H. M.; Kendrick, R. D. *Science* **1994**, *264*, 1560.
(6) Schaff, A.; Veeman, W. S. *Appl. Phys. Lett.* **1997**, *70*, 2598.
(7) Kundla, E.; Samoson, A.; Lippmaa, E. *Chem. Phys. Lett.* **1981**, *83*, 229.
(8) Kentgens, A. P. M. *Prog. NMR Spectrosc.* **1998**, *32*, 141.

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