UNEXPECTED LINE-NARROWING AND SENSITIVITY ENHANCEMENT AT HIGH FIELDS IN MAGIC ANGLE SPINNING NMR OF SPIN-1/2 NUCLEI IN SOLIDS

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Introduction

Advantages of very high fields in nuclear magnetic resonance (NMR) include the improved sensitivity, increased chemical shift dispersion, reduced second-order quadrupolar interactions, improved relaxation properties, and many others. Such advantages have been well demonstrated for liquids and for aligned samples. For quadrupolar nuclei in solids, the line-narrowing effects are at least quadratic with the static magnetic field, B_0, because of the combination of the chemical shift dispersion and the reduction of the second-order line broadening at high fields. However, the situation is less clear for spin-1/2 nuclei in solids, related in part to bulk magnetic susceptibility line broadening effects [1], which also scale with B_0. One technique that is proving highly useful for minimizing the magnetic susceptibility effects in solids is magic angle spinning (MAS) of a single crystal [2], especially as applied to the study of solid-solid phase transitions in which the resolution enhancement is crucial. It is thus of interest to examine if high fields do provide an improvement in resolution in MAS NMR measurements of spin-1/2 nuclei, using the highest available ultra-wide bore 900 MHz NMR spectrometer, currently operating at 21.1 T.

Experimental

A ^{15}N-labled $NH_4H_2AsO_4$ (henceforth, ADA) single crystal, an interesting antiferroelectric material [3], was used in this study. The ^{15}N CP/MAS NMR measurements were performed in different NMR spectrometers (Bruker DMX 300, Bruker Avance 600, and ultra-wide bore 900 MHz). A small piece of ADA single crystal was packed in a 4-mm MAS rotor and used for NMR measurements on 300 and 600 MHz, while a slightly smaller size of the ADA crystal was packed in a 3.2-mm MAS rotor for the measurements on 900 MHz.

Results and Discussion

Fig. 1 shows the ^{15}N CP/MAS NMR spectra of the ADA single crystal recorded at different static fields (7.0, 14.1, and 21.1 T). The transverse relaxation time T_2 was measured to be 138, 160, and 163 ms for 7.0, 14.1, and 21.1 T, respectively. The ^{15}N line-widths of ADA decrease nonlinearly on going from 7.0 to 21.1 T (0.260 ppm to 0.071 ppm, respectively), which can be attributed to an increase in the spin-spin relaxation time, T_2. This high field line-narrowing effect not only results in spectral resolution enhancement but also leads to an improvement of the sensitivity beyond what is expected from the $(B_0)^{3/2}$ effect. The signal-to-noise ratio (S/N) measured from the spectra in Fig. 1 was 9, 20, and 41 for 7.0, 14.1, and 21.1 T, respectively. Detailed analyses of the measured S/N estimate an extra enhancement, beyond the $(B_0)^{3/2}$ effect, of a factor of 1.6 and 2.7 by going from 7.0 to 14.1 and to 21.1 T.

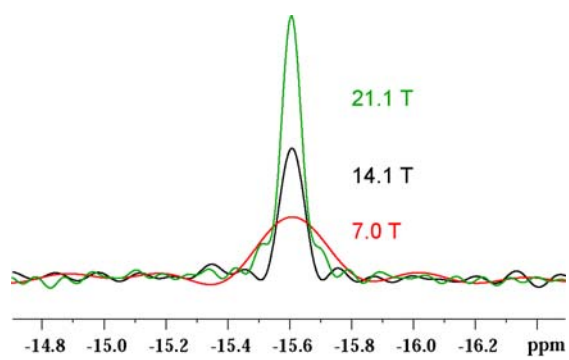

Figure 1. Field Dependence of ^{15}N CP/MAS spectra of an ADA single crystal at 300K at a spinning rate of 2.5 kHz. The spectra were accumulated with 512, 128, and 32 scans using a recycle delay of 10 s on Bruker DMX300 (Red), DRX600 (Black), and the ultra-wide bore 900 NMR spectrometer (Green), respectively. No line-broadening was applied to these spectra. The chemical shift was referenced to ^{15}N isotropy of powdered valine at 0 ppm. The signals were normalized to 32 scans. No spinning sidebands were observed in these spectra.

Conclusions

We have observed a very significant enhancement in NMR resolution and sensitivity at 21.1 T , over and above the expected values, that indicate potential for new applications in materials science.

References

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[3] Gunaydin Sen, O., *et. al.*, Ferroelectrics, **337**, 153-160 (2006).