Communication

Thermometers for low temperature Magic Angle Spinning NMR

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ABSTRACT

The measurement of temperature in a Magic Angle Spinning NMR probe in the temperature range 85–300 K is discussed. It is shown that the shift of the [119]Sn resonance of $Sm_2Sn_2O_7$ makes a good thermometer with shift being given by $\delta = 223 - 9.54 \times 10^4/T$ ppm and a potential precision of better than 0.5 K over the entire temperature range. The sensitivity is such (e.g. 4.2 ppm/K at 150 K) that small temperature gradients across the sample can readily be measured. Furthermore, since the spin–lattice relaxation time is very short, measurements can be made in ~1 s enabling relatively rapid temperature changes to be followed. Values for the chemical shift of [207]Pb in $Pb(NO_3)_2$ down to ~85 K are also presented. Although the [207]Pb shift variation is approximately linear near room temperature (we find a slope 0.725 ± 0.002 ppm/K over the range 293–153 K), it clearly deviates from linearity below ~130 K.

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1. Introduction

Measurement of the sample temperature in a Magic Angle Spinning (MAS) NMR experiment is not straightforward since it can be affected by frictional and rf heating, as well as by the temperature of the gases used for drive and bearing. In addition the temperature may be non-uniform across the sample. Several NMR thermometers have been developed for temperatures around room temperature (~200 to 400 K), principal amongst these is the [207]Pb shift of $Pb(NO_3)_2$ [1] which varies approximately linearly with temperature in this region, although differing values for the linear coefficient from 0.70 [2] to 0.775 [3] ppm/K have been reported, probably due in part to the different range of temperatures used for the calibration. Moreover a high temperature calibration [4] clearly showed the non-linear nature of the shift variation over this more extended temperature range. Low temperature solid-state MAS NMR experiments are increasingly important for various experiments including solid-state DNP, the study of paramagnetically doped samples and to enhance NMR sensitivity. Thus there is a need for a reliable accurate NMR thermometer which can be used down to near liquid N_2 temperatures. Very recently Thurber and Tycko [5] have shown that the T_1 of [79]Br in KBr can be used between 20 and 320 K although, as discussed herein, its accuracy is highest at low temperatures. Also the indicated temperature will be an average over the sample, whereas for a shift-based thermometer the temperature gradient can be directly determined from the width of the NMR line.

In this communication we report a thermometer which uses the shift of the [119]Sn resonance of $Sm_2Sn_2O_7$ first reported by Grey et al. [6] and show that it is able to provide rapid, sensitive and accurate measurements of temperature in an MAS probe down to ~85 K. We also extend the calibration of the [207]Pb shift in $Pb(NO_3)_2$ to lower temperatures than reported hitherto.

2. Experimental

2.1. Sample preparation

A polycrystalline sample of $Sm_2Sn_2O_7$ was prepared by the solid-state reaction of stoichiometric ratios of high purity (99.9+ % pure) SnO_2 with Sm_2O_3. The mixture was finely ground and reacted at 1100 °C for 24 h initially. This was followed by reactions at 1400 °C for 5 days with two intermediate grindings to ensure good homogeneity. X-ray powder diffraction studies on the resulting powder showed it to be single phase with the desired pyrochlore structure.

2.2. NMR experiments

The experiments were conducted using a Varian 600 MHz spectrometer with a modified extended temperature range Direct Insert Doty Scientific 4 mm probe spinning a silicon nitride rotor at 5 kHz. The [119]Sn spectra obtained were acquired at 223.7 MHz using one pulse acquisition (pulse length 60°), a repetition time of 0.01 s and 100 acquisitions (i.e. ~1 s measurement time). The [207]Pb NMR experiments were conducted at 125.5 MHz using a single 60° pulse with a repetition rate which changed between 30 and 300 s depending on temperature. The T_1 measurements of [79]Br (at 150.3 MHz) in KBr used a saturation recovery experiment with 1 acquisition per delay and at least 100 delay increments varying from 0.25 to 5 ms depending on the temperature, typically taking several minutes.

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Shift referencing was conducted by using the known shift of $Pb(NO_3)_2$ and $Sm_2Sn_2O_7$ samples at 293 K [1,6]. The isotropic line for $Sm_2Sn_2O_7$ was identified by varying the spinning speed and noting which line's position was independent of spinning rate.

The Doty Scientific probe uses cooled bearing and drive gases from a heat exchanger immersed in liquid nitrogen. The pressures were controlled using a Varian spin rate controller and the temperature was controlled using a Doty temperature controller. The temperature of the drive and bearing gas are measured independently as they enter the stator and the temperature was corrected using resistive heaters just before the thermocouples. The bearing gas is the main source of cooling for the sample. The drive, which acts on the top cap, has only a small effect on the temperature, being cooled and controlled independently to the bearing. The PID temperature controller allows the temperature to be stabilised to $\sim\pm0.5$ K. The temperature stabilisation was checked by the repeatability of the shift of the ^{119}Sn and ^{207}Pb resonances. A stable sample temperature (as indicated by a constant value for the shift) was always achieved within 30 s of the temperature stabilising on the temperature controller and 60 s delay was used before conducting all low temperature experiments. Frictional heating of the sample due to spinning was measured using the shifts of both $Pb(NO_3)_2$ and $Sm_2Sn_2O_7$ as a function of spinning speed at room temperature and was found to be approximately 2 K when spinning at 5 kHz.

3. Results

3.1. $Sm_2Sn_2O_7$

Fig. 1 shows ^{119}Sn MAS NMR spectra of samarium stannate at different temperatures as indicated by the bearing temperature of the probe with the arrow denoting the isotropic shift. As the width of the spinning side band manifold does not vary significantly with temperature, the isotropic shift remains easy to pick out. The T_1 of ^{119}Sn drops approximately linearly with temperature over the range 300–90 K, with T_1 being 2.4 ms at 300 K and $\sim$0.7 ms at 90 K ($T_1 \sim 7 \times 10^{-6} T$ s). The very short T_1 allows very rapid experiments to be conducted so that snap shots of temperature can be acquired in less than 1 s throughout the temperature range.

Fig. 2 shows the temperature dependence of the ^{119}Sn shift. As the temperature dependent part of the shift, K, in samarium stannate will be dominated by the hyperfine interaction with the Sm^{3+} ion, one expects that $K = H_{hfs}\chi$, where χ is the magnetic susceptibility of the sample and H_{hfs} is the hyperfine field strength. The susceptibility of samarium stannate is expected to vary in a Curie
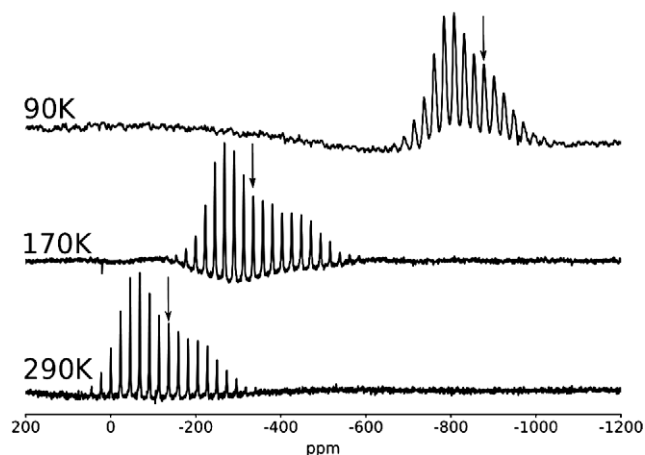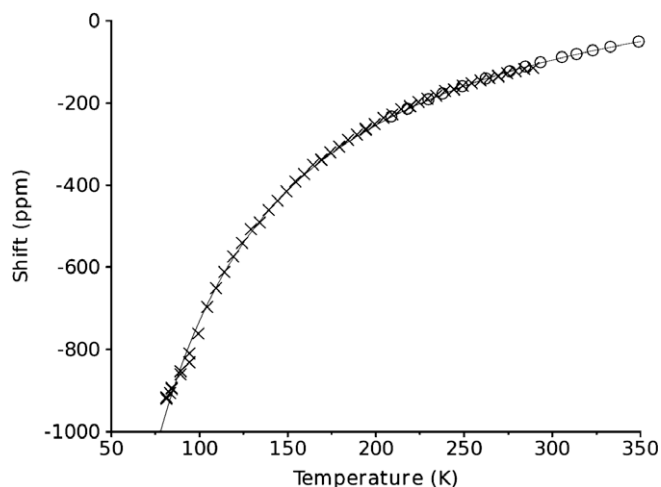

Fig. 2. ^{119}Sn shift in $Sm_2Sn_2O_7$ plotted against temperature, crosses are our data and the circles are Grey et al. data. Line is shift (ppm) = −95364/T + 223.

like manner i.e. inversely with temperature and the line through the data shows a fit to Eq. (1).

$$\delta = 223 - 9.54 \times 10^4 / T \tag{1}$$

This is an excellent fit ($R^2 = 0.999$) and is also in very good agreement with the more limited higher temperature data of Grey et al. who found $\delta = 223 - 9.53 \times 10^4 / T$ between 209 and 349 K.

The spin–lattice relaxation time for ^{79}Br in KBr was found by Thurber and Tycko [5] to fit the following empirical expression to within 5% between 20 and 296 K:

$$T_1 = 0.0145 + 5330 T^{-2} + (1.42 \times 10^7) T^{-4} + (2.48 \times 10^9) T^{-6} \tag{2}$$

We have therefore used this as a check on the temperature as indicated by the ^{119}Sn shift (Eq. (1)). The temperatures predicted from the ^{119}Sn shift and the ^{79}Br T_1 are plotted against the bearing temperature of the probe, together with the temperature predicted from the ^{207}Pb shift using 0.753 ppm/K (the most commonly used value) [1,7] in Fig. 3a. The solid line is for the calculated temperature matching the bearing temperature. At temperatures above 200 K all NMR thermometers agree and lie on the solid line to within error. At lower temperatures the ^{79}Br T_1 in KBr and the ^{119}Sn shift in $Sm_2Sn_2O_7$ still agree with the indicated bearing temperature, however, a linear extrapolation of the ^{207}Pb shift in lead nitrate to lower temperature starts to deviate from these readings, being about 15 K too high at 90 K. This indicates that the ^{207}Pb shift begins to change more slowly with temperature below $\sim$150 K. The linear change in chemical shift with temperature around room temperature for lead nitrate is thought to come mainly from the thermal contraction of the unit cell [8]. Presumably the slower rate of change of shift with temperature below 150 K comes from a lower rate of thermal contraction at lower temperatures. Fig. 3b shows the shift of ^{207}Pb down to 85 K where the departure from linearity can be clearly seen below $\sim$130 K. At temperatures above 153 K a linear fit to the data gives a slope of 0.725 ± 0.002 ppm/K, very close to the value of 0.712 ppm/K over a slightly larger temperature range reported recently in the supplementary data of [9] (the reason for their slightly smaller slope is that we did not include data below 150 K, where the non-linearity begins to increase, in the fit).

4. Discussion

Fig. 4 shows the potential precision of each of the thermometers discussed in this paper. This is based upon a 5% error in the T_1 mea-
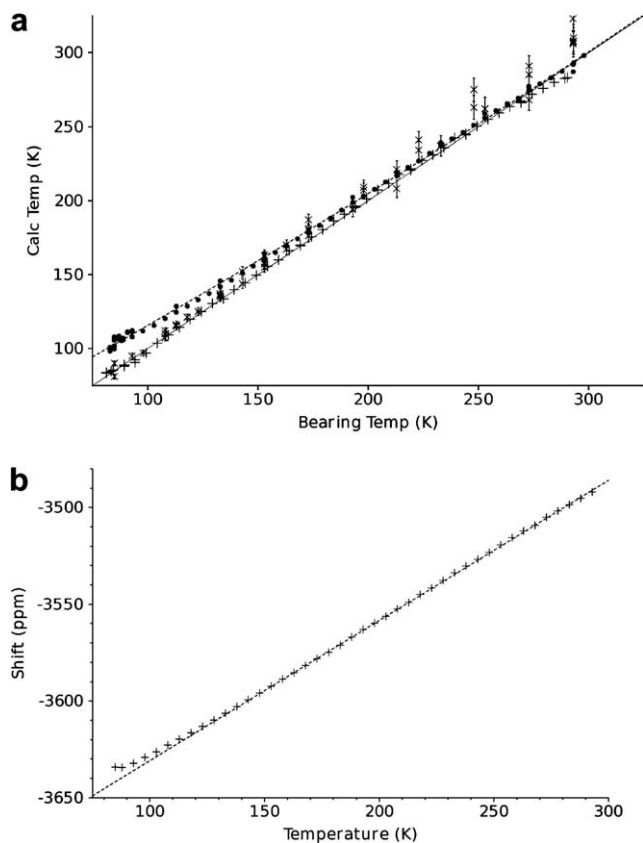

Fig. 1. ^{119}Sn MAS NMR spectra of $Sm_2Sn_2O_7$ at top 90 K, middle 170 K, and bottom 290 K.

Fig. 3. (a) Bearing temperature of probe plotted against calculated temperature for the different thermometers (circles: $Pb(NO_3)_2$ [1], crosses KBr [5] and plusses $Sm_2Sn_2O_7$), (b) [207]Pb chemical shift for $Pb(NO_3)_2$ as a function of temperature.

surements for KBr as, although individual fits may have high levels of accuracy, it is very difficult to obtain a repeatability of better than 5% between experiments. The errors for both the $Pb(NO_3)_2$ and the $Sm_2Sn_2O_7$ are based upon the error in shift position due to the linewidth. For $Pb(NO_3)_2$, where the linewidth of our sample is ~0.6 ppm, the error in the shift is taken as 0.2 ppm. For $Sm_2Sn_2O_7$ there is a significant contribution to the width from T_1 at lower temperatures so that the [119]Sn linewidth is temperature dependent and thus the error in shift measurement changes with temperature. The residual linewidth for our sample is approximately 1.3 ppm and the contribution from T_1 due to the approxi-
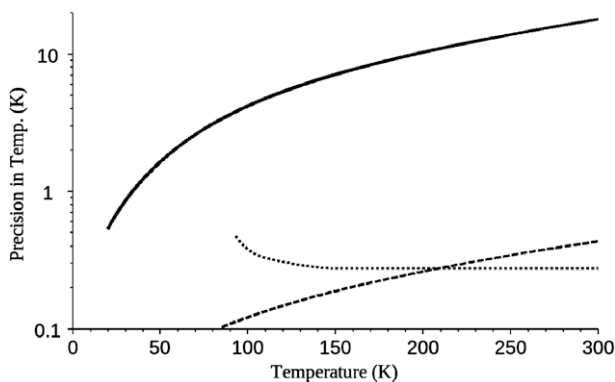

Fig. 4. Theoretical precision of thermometers based on 0.2 ppm shift error for $Pb(NO_3)_2$, 0.2 of the linewidth (including residual linewidth and contribution due to T_1) for $Sm_2Sn_2O_7$ and a 5% error in [79]Br T_1 for KBr. Dashed line $Sm_2Sn_2O_7$, dotted line $Pb(NO_3)_2$, solid line KBr.

mate linear relation of T_1 with temperature is such that at 150 K the width is ~4 ppm. We have taken the 'uncertainty' in shift as 0.2 of the linewidth.

It can be seen that the precision in temperature measurement is least when using the [79]Br T_1 (~18 K at *RT*) but becomes significantly better as the temperature is reduced (~4 K at 100 K). This is partly because of the accuracy of expression (2) and of the difficulty of measuring T_1 to high accuracy, but also because the spin–lattice relaxation time varies more rapidly at low temperature. The potential precision using the [207]Pb shift is ~0.3 K down to ~150 K, as the shift of [207]Pb varies linearly with temperature in this range. Below ~150 K the precision slowly worsens as the shift change with temperature decreases, giving an approximate accuracy of ~0.5 K at 93 K. For [119]Sn the potential precision is better than 0.5 K at all temperatures from 300 K downwards. The precision improves at lower temperature because the increased sensitivity, from ~1.1 ppm/K at 300 K to 9.5 ppm/K at 100 K, more than compensates for the extra linewidth from T_1. Thus below ~200 K the [119]Sn shift becomes the most accurate of these thermometers (as well as the fastest).

The discussion above assumes that the temperature gradient over the sample is insignificant. This can be readily checked using the width of the [119]Sn or [207]Pb line. In our probe it begins to make a significant difference to the width at ~125 K where the temperature gradient across the sample is ~0.6 K and both [207]Pb and [119]Sn agree that at 85 K the temperature gradient across the sample is <1 K. The high sensitivity of [119]Sn means that at the lowest temperatures of operation of our probe (~85 K) the temperature differential across the sample can make [119]Sn more difficult to use as a thermometer. For instance if the temperature differential across the sample were approximately 0.8 K at 85 K the increased linewidth (12.4 ppm) would mean that the sideband pattern would begin to merge when spinning at 5 kHz (for [119]Sn frequency 223.7 MHz).

An advantage of using KBr is that it is very sensitive so a small (<10%) amount can be packed along with the sample [5] and used as a real time thermometer (albeit with a measurement time of several minutes). Although the [119]Sn signal in $Sm_2Sn_2O_7$ is smaller than that of [79]Br, because of the very short relaxation time, it should also be possible to use $Sm_2Sn_2O_7$ in a diluted form together with the sample of interest provided that the temperature is sufficiently stable.

5. Conclusion

The shift of [119]Sn in $Sm_2Sn_2O_7$ makes an excellent temperature sensor for MAS NMR below room temperature. The large change of shift with temperature means that the potential precision is better than 0.5 K throughout the temperature range down to ~85 K and the short T_1 makes measurements very fast (<~1 s). In fact we were able to study variations in temperature of ~1 K over a minute in our probe at 90 K. The ability to measure temperature variations on the time scale of seconds is a significant advantage when developing low temperature MAS technology.

A straightforward linear extrapolation of the [207]Pb shift in $Pb(NO_3)_2$ to temperatures below ~150 K is shown to be incorrect. However, provided that the shift vs. *T* data presented here are used, $Pb(NO_3)_2$ is perfectly adequate as a temperature sensor down to ~90 K although rapid temperature changes cannot be followed effectively due to the very long T_1. The use of [79]Br T_1 in KBr gives the lowest precision (~4 K at 100 K, ~10 K at ~200 K), however, it has the advantage for those interested in ^{13}C NMR that its Larmor frequency is very close to ^{13}C and only a slight probe retuning is necessary. A disadvantage of a relaxation time rather than a shift thermometer is that temperature gradients across the sample

cannot be measured and these, if significant, are most likely to be important at lower temperatures in an MAS probe. Hence $Sm_2Sn_2O_7$ has been shown to be a practical NMR thermometer for solid-state NMR. It produces rapid high precision temperature measurements from room temperature down to 85 K and it can be used to characterise temperature gradients across the sample and fluctuations in temperature on a ~1 s timescale.

Acknowledgments

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