Communication

Thermometers for low temperature Magic Angle Spinning NMR

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A B S T R A C T

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$_2$Sn$_2$O$_7$ 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 of 0.725 ± 0.002 ppm/K over the range 293–153 K), it clearly deviates from linearity below ~130 K.

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 ($\sim$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$_2$Sn$_2$O$_7$ 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$_2$Sn$_2$O$_7$ was prepared by the solid-state reaction of stoichiometric ratios of high purity (99.9+% pure) SnO$_2$ with Sm$_2$O$_3$. 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 300 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(NO₃)₂ and Sm₂Sn₂O₇ samples at 293 K [1,6]. The isotropic line for Sm₂Sn₂O₇ 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 ±0.5 K. The temperature stabilisation was checked by the repeatability of the shift of the ¹¹⁹Sn and ²⁰⁷Pb resonances. A stable samarium stannate will be dominated by the hyperfine interaction with the Sm³⁺ ion, one expects that \( K = H_{hf}X \), where \( X \) is the magnetic susceptibility of the sample and \( H_{hf} \) is the hyperfine field strength. The susceptibility of samarium stannate is expected to vary in a Curie like manner i.e. inversely with temperature and the line through the data shows a fit to Eq. (1).

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\delta = 223 - 9.54 \times 10^4/T 
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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 \( \delta = 223 - 9.53 \times 10^3/T \) between 209 and 349 K.

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

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

We have therefore used this as a check on the temperature as indicated by the ¹¹⁹Sn shift (Eq. (1)). The temperatures predicted from the ¹¹⁹Sn shift and the ⁷⁹Br \( T_1 \) are plotted against the bearing temperature of the probe, together with the temperature predicted from the ²⁰⁷Pb shift using 0.753 ppm/K (the most commonly used value, \( 9.53 \times 10^3/\text{T} \)) 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 ⁷⁹Br \( T_1 \) in KBr and the ¹¹⁹Sn shift in Sm₂Sn₂O₇ still agree with the indicated bearing temperature, however, a linear extrapolation of the ²⁰⁷Pb 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 ²⁰⁷Pb shift begins to change more slowly with temperature below ~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 ²⁰⁷Pb down to 85 K where the departure from linearity can be clearly seen below ~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).

Fig. 1 shows ¹¹⁹Sn 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 ¹¹⁹Sn drops approximately linearly with temperature over the range 300–90 K, with \( T_1 \) being 2.4 ms at 300 K and ~0.7 ms at 90 K \((T_1 \sim 7 \times 10^{-6} \text{s})\). The very short \( T_1 \) allows very rapid experiments to be conducted so that snapshots of temperature can be acquired in less than 1 s throughout the temperature range.

Fig. 2 shows the temperature dependence of the ¹¹⁹Sn shift. As the temperature dependent part of the shift, \( K \), in samarium stannate will be dominated by the hyperfine interaction with the Sm³⁺ ion, one expects that \( K = H_{hf}X \), where \( X \) is the magnetic susceptibility of the sample and \( H_{hf} \) is the hyperfine field strength. The susceptibility of samarium stannate is expected to vary in a Curie

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Fig. 2 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-
measurements 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(NO₃)₂ and the Sm₂Sn₂O₇ are based upon the error in shift position due to the linewidth. For Pb(NO₃)₂, where the linewidth of our sample is ~0.6 ppm, the error in the shift is taken as 0.2 ppm. For Sm₂Sn₂O₇ there is a significant contribution to the width from T₁ at lower temperatures so that the ¹¹⁹Sn 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 T₁ due to the approximately linear relation of T₁ 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 ⁷⁹Br ¹¹⁹Sn (~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 T₁ to high accuracy, but also because the spin–lattice relaxation time varies more rapidly at low temperature. The potential precision using the ²⁰⁷Pb shift is ~0.3 K down to ~150 K, as the shift of ²⁰⁷Pb 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 ¹¹⁹Sn 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 T₁. Thus below ~200 K the ¹¹⁹Sn 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 ¹¹⁹Sn or ²⁰⁷Pb 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 ²⁰⁷Pb and ¹¹⁹Sn agree that at 85 K the temperature gradient across the sample is <1 K. The high sensitivity of ¹¹⁹Sn means that at the lowest temperatures of operation of our probe (~85 K) the temperature differential across the sample can make ¹¹⁹Sn 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 ¹¹⁹Sn 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 ¹¹⁹Sn signal in Sm₂Sn₂O₇ is smaller than that of ⁷⁹Br, because of the very short relaxation time, it should also be possible to use Sm₂Sn₂O₇ in a diluted form together with the sample of interest provided that the temperature is sufficiently stable.

5. Conclusion

The shift of ¹¹⁹Sn in Sm₂Sn₂O₇ 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 T₁ 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 ²⁰⁷Pb shift in Pb(NO₃)₂ to temperatures below ~150 K is shown to be incorrect. However, provided that the shift vs. T data presented here are used, Pb(NO₃)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 T₁. The use of ⁷⁹Br T₁ 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 ¹³C NMR that its Larmor frequency is very close to ¹³C 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$_2$Sn$_2$O$_7$ 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 $\sim$1 s timescale.

Acknowledgments

This work was supported by an EPSRC (UK) Basic Technology Project, EP/D045967. We thank Doty Scientific Inc. for their cooperation in the development of the MAS probe used for this work.

References


