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Communication

A Hall effect angle detector for solid-state NMR

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Abstract

We describe a new method for independent monitoring of the angle between the spinning axis and the magnetic field in solid-state NMR. A Hall effect magnetic flux sensor is fixed to the spinning housing, so that a change in the stator orientation leads to a change in the angle between the Hall plane and the static magnetic field. This leads to a change in the Hall voltage generated by the sensor when an electric current is passed through it. The Hall voltage may be measured externally by a precision voltmeter, allowing the spinning angle to be measured non-mechanically and independent of the NMR experiment. If the Hall sensor is mounted so that the magnetic field is approximately parallel to the Hall plane, the Hall voltage becomes highly sensitive to the stator orientation. The current angular accuracy is around 10 millidegrees. The precautions needed to achieve higher angular accuracy are described.

Keywords: Magic-angle spinning; Hall effect; NMR; Solid-state NMR

1. Introduction

Many solid-state NMR experiments require precise knowledge of the relative orientation of the magnetic field and the sample container. For example, the NMR signals of oriented samples depend strongly on the sample orientation with respect to the field, and this angular dependence may be used to determine the orientation of spin interaction tensors with respect to a molecular reference frame, or with respect to an external order axis [1–3]. The NMR of spinning samples, including unoriented powders, is often very sensitive to the angle between the spinning axis and the magnetic field [4–13]. Methods such as satellite-transition magic-angle spinning (ST-MAS) may be sensitive to changes in the spinning angle of the order of a few millidegrees [6–9]. Several techniques involve spinning the sample about an axis which is slightly offset from the magic angle with respect to the magnetic field (off-MAS) [10–13]. For example, the spin echoes of coupled spin systems in solids, taken under off-MAS conditions, display modulations due to residual dipole–dipole couplings [13]. The residual dipolar effects are analogous to those observed in slightly anisotropic liquids, which are widely used in biomolecular structural studies [14].

There are several NMR methods for determining the orientation of the sample holder, or the sample rotor, with respect to the magnetic field. For example, in magic-angle-spinning NMR, it is common practice to use the ^{79}Br resonance of KBr to set the orientation of the rotation axis by maximizing the number of satellite transition rotational echoes. Having set the spinning angle, the KBr sample is exchanged with the sample of interest, hopefully without significant mechanical disturbance. Spinning angles which are offset from the magic angle may then be set by mechanical adjustments of the stator orientation. In modern NMR probes, sound mechanical design makes this procedure feasible, but not completely reliable. Changes in temperature

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and gas pressure may still lead to small angle changes which are undetected until the NMR data is analyzed.

There is a clear need for an *NMR-independent* method of detecting the angle of the sample holder or stator with respect to the magnetic field. Early attempts were made to monitor the stator orientation by reflecting a laser beam off a polished surface [15]. However, this method proved to be too unreliable for routine use.

In this report, we explore the use of the *Hall effect* for angular estimations. When an electric current is passed through a semiconductor in a magnetic field, a potential difference, or *Hall voltage* V_H is developed, perpendicular to both the current and the magnetic field [16]. This voltage is a manifestation of the Lorentz force on moving charge carriers. The Hall effect is routinely exploited for measuring the strength of magnetic fields, and commercial devices are available with suitable characteristics at typical NMR field strengths and temperatures. We now show that when mounted in an unconventional geometry, commercial Hall effect devices may also be used to estimate the orientation of the NMR sample holder with respect to the magnetic field.

2. A Hall effect angle sensor

A Hall effect device consists of a small rectangular plane of semiconductor material, with four leads connected at the edges. A well-defined current I_c is passed between two opposite poles of the device, while the Hall voltage V_H is monitored between the two other poles using an accurate voltmeter (see Fig. 1). Denote Fig. 1 the normal to the Hall plane by $\mathbf{z}_H$, and the direction of the magnetic field by $\mathbf{z}_L$, where the subscript L denotes the laboratory reference frame. The angle between the vectors $\mathbf{z}_H$ and $\mathbf{z}_L$ is denoted fiHL. The Hall voltage is given by

$$V_H \cong V_H^0 + \frac{I_c B}{q\rho d} \cos\beta_{HL} \quad (1)$$

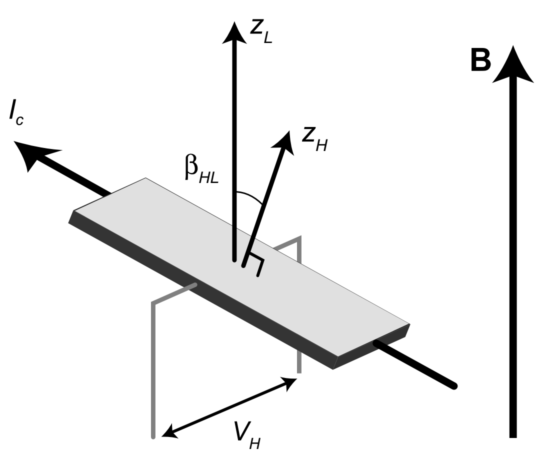

Fig. 1. In the Hall effect, a supply current I_c is passed through the Hall device, while the voltage V_H is measured perpendicular to the current. The Hall voltage is proportional to $\cos\beta_{HL}$, where β_{HL} is the angle between the normal to the Hall plane $\mathbf{z}_H$ and a vector parallel to the magnetic field $\mathbf{z}_L$.

where ρ is the density of charge carriers in the material, q is the charge on the current carriers, B is the magnetic flux density at the device, d is the thickness of the semiconductor plane. In well-designed devices, the offset voltage V_H^0 is orders of magnitude smaller than the magnetically-generated Hall voltage. Devices may be constructed for which Eq. (1) is satisfied with high accuracy for magnetic flux densities up to more than 20 T.

The work described below used the sensor HGCT-3020 from Lakeshore Cryotronics, Westerville, Ohio, USA (www.lakeshore.com). The dimensions of the sensor housing are 16 mm × 6.1 mm × 1.1 mm, allowing to be readily accommodated inside an NMR probe. The active area of the sensor is only around 1 mm^2. The sensor is designed to operate with a control current of $I_c = 100$ mA in which case the magnetic sensitivity $I_c = q\rho d$ is specified to be between 5.5 and 10.5 mV T^{-1}, the precise value to be determined by calibration. The operational temperature range is very wide (4.2–375 K) with a temperature coefficient in the magnetic sensitivity of only 10 with deviations from linearity kept below 2% for fields up to 15 T. The Hall offset V_H^0 is specified to be less than 200 μV in magnitude, with a temperature coefficient of less than 0.4 μV K^{-1}. These parameters are important when assessing the accuracy of the estimated angle (see below).

Normally, a Hall sensor is mounted in the perpendicular geometry. This means that the semiconductor plane is oriented so that the normal to the plane is parallel to the magnetic field ($\beta_{HL} \cong 0$, see Fig. 2a). In this geometry, Fig. 2 Hall voltage is proportional to the magnetic flux density B, and is insensitive to small changes in the angle β_{HL}.

For the work described here, an unconventional parallel geometry is used instead, in which the Hall plane is oriented parallel to the magnetic flux lines ($\beta_{HL} \cong \pi/2$, see Fig. 2b). In this case, the Hall voltage is close to zero and depends strongly on the angle β_{HL}. In NMR experiments, the magnetic flux density is known with great accuracy and is highly stable, so only the angular dependence is important.

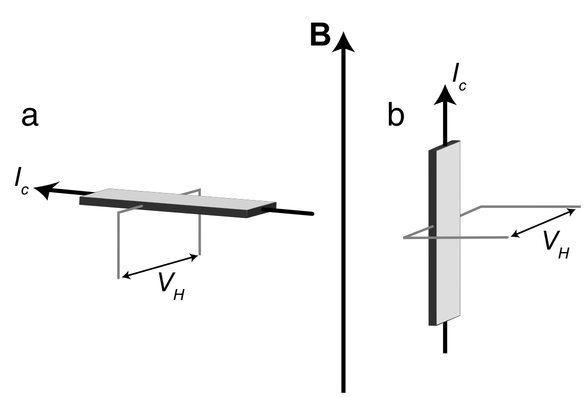

Fig. 2. In the conventional perpendicular geometry (a), the Hall plane is perpendicular to the magnetic field. In the work described here we use the parallel geometry (b), in which the magnetic field is parallel to the Hall plane.

Consider the problem of determining the angle between the spinning axis, in a magic-angle-spinning experiment. It is, of course, not possible to attach the Hall device and its current leads to the rotor itself. Instead, the Hall device is fixed to the stator, in such a way that a change in the stator orientation leads to a change in the relative orientation of the Hall plane and the magnetic field, and hence a change in the Hall voltage. Since the gas bearings on which the rotor is supported have a machined precision of microns, and a clearance of tens of microns, the time-average rotor axis is expected to follow the orientation of the stator to a precision of less than a thousandth of a degree.

For maximum angle sensitivity, the Hall device is mounted to the stator in such a way that the Hall plane is approximately parallel to the magnetic field when the rotor axis is at the magic angle. In our case we used a carefully machined attachment, to fix the Hall device to the stator, as shown in Fig. 3. If Fig. 3 the rotor axis is denoted $\mathbf{z}_\mathrm{R}$, the angle between the normal to the Hall plane $\mathbf{z}_\mathrm{H}$ and the rotor axis is denoted β_HR. Ideally this angle is equal to 35.2644°, i.e.

$$\beta_\mathrm{HR} \cong \pi/2 - \arctan\sqrt{2} \tag{2}$$

In practice, β_HR is likely to deviate from the ideal angle by a degree or so.

For simplicity, assume that $\mathbf{z}_\mathrm{H}$, $\mathbf{z}_\mathrm{R}$, and the magnetic field $\mathbf{B}$, are all approximately in the same plane. The angle between the normal to the Hall plane and the magnetic field is given by

$$\beta_\mathrm{HR} \cong \beta_\mathrm{HR} + \beta_\mathrm{RL} \tag{3}$$

where the relationship is exact if all vectors are in the same plane. The angle between the normal to the Hall plane and the magnetic field is given by

$$\beta_\mathrm{HR} \cong \pi/2 + \Delta \tag{4}$$

where Δ is the misset of the rotor axis from the magic angle:

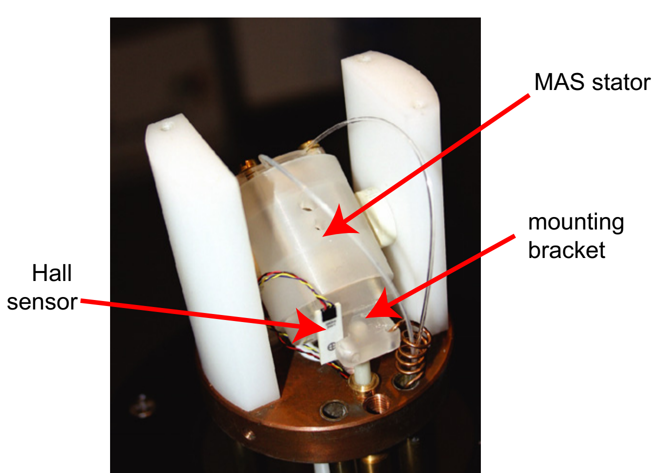

Fig. 3. Photograph of the magic-angle-spinning assembly showing the Hall sensor and the mounting bracket.

$$\Delta = \beta_\mathrm{RL} - \arctan\sqrt{2} \tag{5}$$

With these assumptions, we may write

$$\cos\beta_\mathrm{HL} \cong -\Delta + \epsilon \tag{6}$$

where ϵ is a small angle, which takes into account the inevitable inaccuracy in mounting the Hall device, and small deviations from the co-planarity of $\mathbf{z}_\mathrm{H}$, $\mathbf{z}_\mathrm{R}$ and $\mathbf{z}_\mathrm{L}$.

With these assumptions, the Hall voltage is given for small values of the angle offset Δ by

$$V_\mathrm{H}(\Delta) = V_\mathrm{H}(0) - \frac{I_\mathrm{c}B}{q\rho d}\Delta \tag{7}$$

where $V_\mathrm{H}(0)$ is the Hall voltage when the spinning axis is exactly at the magic angle to the field:

$$V_\mathrm{H}(0) = V_\mathrm{H}^0 + \frac{I_\mathrm{c}B}{q\rho d}\epsilon \tag{8}$$

In practice, $V_\mathrm{H}(0)$ may be determined by a calibration experiment, using a sensitive NMR method for detecting when the spinning axis is exactly at the magic angle. Once this calibration is performed, the angle offset Δ may be determined directly from the Hall voltage, using the linear relationship in Eq. (7).

For the Lakeshore HGCT-3020 in the parallel geometry, the angle sensitivity of the Hall voltage $I_\mathrm{c}B/q\rho d$ in a magnetic field of $B = 9{:}395$ T is between 52 and 99 mV rad^{-1}, corresponding to a range of between 0.9 and 1.7 mV/°. This implies that the Hall voltage changes by around 1 μV for an angle change of one thousandth of a degree. Such voltage changes are readily detectable using an accurate voltmeter.

The achievable accuracy, precision and reproducibility of this angular measurement depends on several factors. Eq. (8) indicates that the stability and accuracy of the current I_c, offset voltage V_H^0, and alignment error ϵ, are all important. In particular, any errors in the alignment error ϵ and current I_c multiply each other. Furthermore, the offset voltage V_H^0 may also depend on temperature and supply current. If we assume that the Hall voltage may be measured to a precision δV_H, that the Hall offset voltage is reproducible within an error margin of δV_H^0, that the supply current is reproducible within an error margin of δI_c, and that the misalignment ϵ is reproducible within an angle $\delta\epsilon$, then the estimated confidence limit on the angle Δ in the vicinity of $\Delta = 0$ is given by

$$\delta\Delta^2 \cong \frac{\delta V_\mathrm{H}^2 + (\delta V_\mathrm{H}^0)^2}{(I_\mathrm{c}B/q\rho d)^2} + \left(\frac{\delta I_\mathrm{c}}{I_\mathrm{c}}\right)^2 + \delta\epsilon^2 \tag{9}$$

Realistically, it is possible to measure the voltage to an accuracy of $\delta V_\mathrm{H} \sim 5$ μV, using standard inexpensive equipment. The Hall offset voltage has a specified temperature sensitivity of less than 20 nV K^{-1}, so δV_H^0 will be negligible for modest temperature variations. A well-designed current source should be stable to a level of $\delta I_\mathrm{c}/I_\mathrm{c} \sim 1\%$, and it should be possible to mount the device with an alignment error ϵ of less than 1°, with a reproducibility and temperature variation of the alignment angle $\delta\epsilon$ of a few millidegrees. Under these conditions, the largest error terms are proportional to δV_H and $\epsilon\delta I_c$, which combine to give around 20 millidegrees accuracy in the angle Δ for routine electronic equipment and ordinary care with mechanical alignment. This estimate is supported by the experimental data given below.

3. Results

The concept was tested by fixing the Lakeshore HGCT-3020 Hall probe to a modified Varian 4 mm magic-angle-spinning stator in the field-parallel geometry, as shown in Fig. 3. The supply current $I_c = 100$ mA was generated by a home-built stabilized current source, with an accuracy of around 1%. The current source was connected to the Hall effect device by a twisted pair of leads, in order to minimize the interference of the supply current I_c with the magnetic field homogeneity at the sample. The Hall voltage was monitored outside the probe by a standard 7-digit voltmeter. This was operated in a time-averaging mode, with an averaging duration of around 1 s, in order to reduce interference from low-frequency ambient electric fields. Initially, we encountered troublesome interference from radio signals picked up by the Hall probe leads and coupled to the NMR receiver circuit. This interference was reduced to acceptable levels by improving the rf shielding of the Hall device leads.

The Hall device was tested by performing NMR experiments over a range of spinning angles, while monitoring the Hall voltage. The spinning angle was varied by turning the usual mechanical drive on the probe base, which rotates the stator around an axis perpendicular to the magnetic field. The true spinning angles were determined by comparing the NMR spectra with SIMPSON simulations [17].

There are many NMR experiments that are extremely sensitive to the spinning angle. For example, the ST-MAS experiment [6–9] is sensitive to deviations from the magic angle by only a few millidegrees. However, a reliable and simple method for determining the spinning angle over a range of around 1° is less easy to find. Accurate simulation of off-MAS lineshapes usually requires accurate knowledge of multiple spin interaction tensors and their relative orientations. We have generally found that literature values are not sufficiently accurate for this purpose. In fact we suspect that off-magic-angle spinning could be a good method to refine estimates of spin interaction parameters.

For our prototype tests, we avoided these issues by using the ^{31}P NMR spectra of trimethyl phosphine sulfide (TMPS, $(CH_3)_3Ps$, see Fig. 4a). The crystal structure of this compound is very simple, with two molecules in the unit cell, related by an inversion operation [18]. There is therefore only a single ^{31}P NMR peak. Furthermore, the phosphorus atoms are located on three-fold rotation axes. This ensures that the chemical shift anisotropy (CSA) tensor is uniaxial ($\eta = 0$). The ^{31}P NMR spectra of this compound are therefore very easy to simulate, with very few unknown parameters. In addition, the methyl proton nuclei in TMPS are relatively easy to decouple and their rapid rotational motion provides a convenient mechanism for ^{31}P spin-lattice relaxation. A disadvantage of TMPS is that the ^{31}P NMR spectra are quite insensitive to the spinning angle in the immediate vicinity of the magic angle. Nevertheless, the sensitivity was found to be sufficient for an initial demonstration.

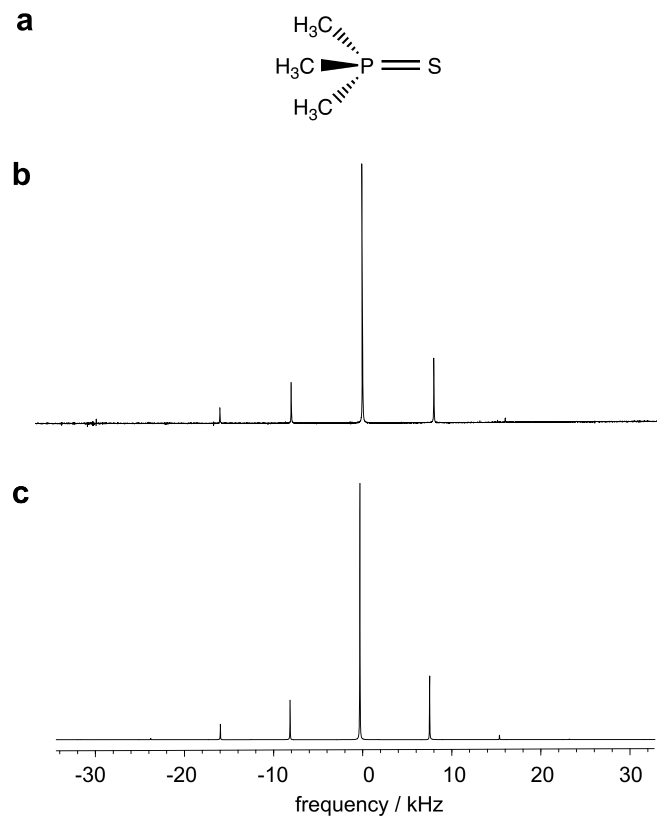

Fig. 4. (a) Molecular structure of TMPS; (b) ^{1}H-decoupled ^{31}P MAS spectrum of trimethyl phosphine sulfide (TMPS) at a spinning frequency of 8.000 kHz and a magnetic field of 9.4 T; (c) numerical simulation using CSA parameters $\delta_{aniso} = 78.8$ ppm, $\eta = 0$, and Lorentzian linebroadening with a width at half-height of 40 Hz.

All the results discussed below concern ^{1}H-decoupled ^{31}P NMR of TMPS obtained in a field of 9.4 T at a magic-angle-spinning frequency of 8.000 kHz. ^{31}P free-induction decays were induced directly using a $\pi/2$ pulse, and observed in the presence of a low-power unmodulated proton decoupler field with an amplitude corresponding to a nutation frequency of $\sim$10 kHz. 32k complex points were acquired using a sample rate of 200 kHz. Consecutive transients were separated by a relaxation delay of 5 s.

The ^{31}P NMR spectrum of TMPS is shown in Fig. 4b. The CSA parameters were determined by fitting the spinning sideband amplitudes to numerical simulations. The best-fit parameters were $\delta_{aniso} = 78.8$ ppm and $\eta = 0$. The corresponding SIMPSON simulation is shown in Fig. 4c. For this and all following simulations, the powder average was computed by using 4180 pairs of orientational Euler angles $\{\alpha, \beta\}$ chosen according to the ZCW algorithm, and 20 values for the third Euler angle γ.

Expanded views of the ^{31}P centrebands taken at three different spinning angles are shown in Fig. 5. The spinning angles were adjusted by changing the stator orientation using the standard mechanical drive, attached to an external knob in the base of the probe. The corresponding voltages on the Hall device are indicated on the plots. In this prototype device, the Hall voltages were stable within around ± 5 μV. The best-fit simulations, obtained by fixing the linewidth to that found at the magic angle, and optimizing the angle misset Δ, are also shown.

Repetition of these results for several angles and two different temperatures allowed construction of the plot in Fig. 6. This shows the observed Hall voltage plotted against the spinning angle offset Δ, as determined by ^{31}P NMR of TMPS. The confidence intervals on the spinning angle offset were determined by plotting the mean square deviation between experiment and simulation, χ^2, against angle offset Δ. The best estimate of the angle offset was determined by localizing the value of Δ providing the minimum of χ^2, i.e. $\chi^2(\Delta) = \chi^2_{\min}$. The confidence limits on Δ were determined by identifying the roots of the equation $\chi^2(\Delta) = \sqrt{2}\chi^2_{\min}$. The confidence limits are considerably wider in the vicinity of the magic angle, $\Delta \approx 0$, compared to large offsets from the magic angle. This is because angle deviations around the magic angle only lead to line broadening, while angle deviations for larger offsets Δ lead to characteristic lineshape distortions.

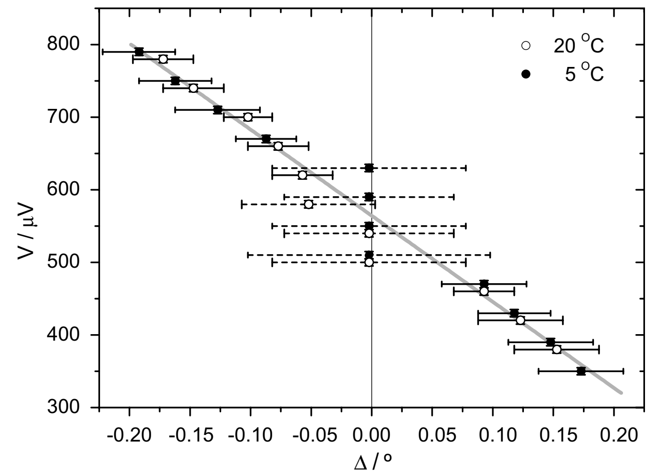

Fig. 6. Measured Hall voltage V_H plotted against magic-angle offset Δ, as determined by the ^{31}P NMR of TMPS, at two different sample temperatures. The error bars in Δ reflect the confidence limits in the NMR determination of Δ, as estimated by individual χ^2 plots for each angle. The confidence limits in V_H reflect the accuracy of the voltmeter. The gray line is the result of a regression analysis, omitting the points near $\Delta = 0$ which have wide confidence limits (dotted error bars).

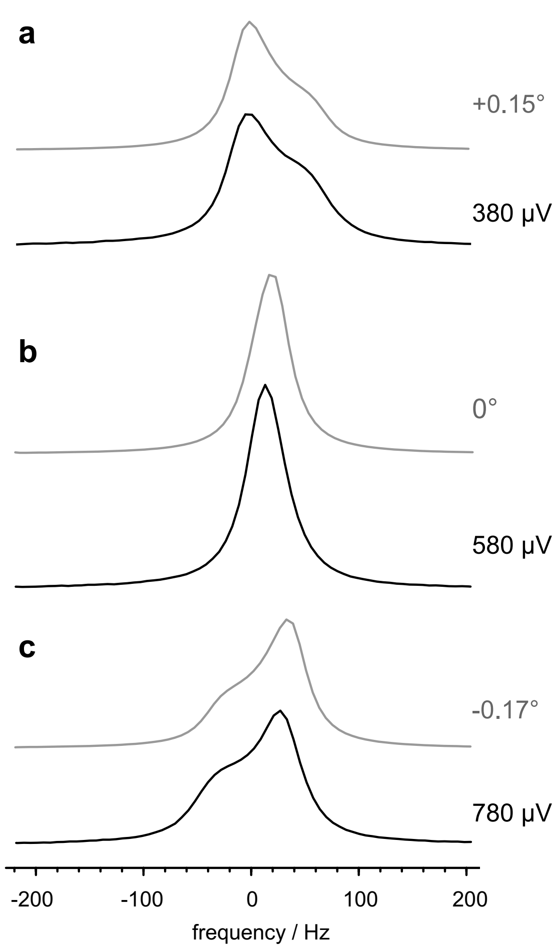

Fig. 5. Centrebands of the ^{1}H-decoupled ^{31}P MAS spectra of TMPS at a spinning frequency of 8.000 kHz at three different missets from the magic angle, and the corresponding Hall voltages. Numerical simulations for the best-fit angle offsets Δ are shown in gray.

A regression analysis, omitting the poorly-defined points near $\Delta = 0$ (dashed error bars in Fig. 6), leads to the gray line in Fig. 6. This corresponds to the relationship

$$V_H(\Delta) = V_H(0) + \frac{dV_H}{d\Delta}\Delta \quad (10)$$

with the following parameters and confidence limits:

$$\begin{aligned} V_H(0) &= 550 \pm 10\ \mu\text{V} \\ \frac{dV_H}{d\Delta} &= -1300 \pm 100\ \mu\text{V}/^\circ \end{aligned} \quad (11)$$

The angle sensitivity parameter $dV_H/d\Delta$ is consistent with the device specifications for $I_c B/q\rho d$. If the Hall offset V_H^0 is neglected, the estimated value of $V_H(0)$ corresponds to an alignment error of $\epsilon \approx 0.42^\circ \pm 0.01^\circ$, which is physically reasonable. The contribution from the offset voltage V_H^0 cannot be determined independently.

Notably, when the sample temperature was changed from 5 to 20 °C, keeping all other settings constant, the Hall voltage changed by around 20 μV. The data in Fig. 6 show that this voltage change reflects a genuine temperature-induced change in the spinning angle, presumably due to differential thermal expansion in the stator mount. Effects of this kind would be very hard to detect on an unknown sample without an NMR-independent monitoring device.

We have performed several more experiments in which the sample temperature and/or spinning frequency were changed. These results were also consistent with the relationship in Eq. (10) within the confidence limits of Eq. (11).

The fit parameters in Eq. (11) indicate that the angle offset Δ may be determined from the Hall voltage V_H with a confidence limit of around 0.01°. This confidence limit is currently determined by the relative insensitivity of the TMPS spectra to the spinning angle, and by the technical specifications of the current source and the voltage measurement device.

4. Conclusions

Initial tests of the Hall effect angle detector are encouraging. The device may be very useful for a wide range of NMR experiments, allowing real-time monitoring and adjustment of the spinning angle without recourse to an independent NMR experiment. At present we estimate the accuracy of the device to be around ±0.01°. We expect that many solid-state NMR spectroscopists will value the presence of a spinning-angle readout that can detect small mechanical or thermal disturbances of the rotor system before an NMR experiment is run.

One of the strengths of this method is that the Hall sensor detects the orientation of the stator or sample holder *with respect to the magnetic field*, not with respect to some external, mechanical, axis system. As a result, the method does not require perfect and reproducible mounting of the probe body inside the magnet, and thermal expansion or contraction of the large probe components will not disturb it.

Higher angle resolution on the order of 1 millidegree is probably achievable but will require stringent precautions with the mechanical alignment and mounting of the Hall device, the provision of a current source with high stability and reproducibility, and the use of a high-resolution and highly stable voltmeter. Improved shielding and stability will also be required for leads connecting the Hall device to the voltmeter. Fixing a temperature sensor to the Hall sensor would allow correction for the temperature-dependence of the device parameters. This may be necessary for high-resolution operation over a wide temperature range.

The Hall voltage could readily be incorporated in a feedback circuit driving a stepper motor for the angle setting, allowing a given spinning angle to be provided on demand. Small changes in the relative orientation of the magnetic field and the stator, generated by passing currents through transverse field coils, could be controlled in a similar way.

The timescale for establishing the Hall voltage is of the order of milliseconds. It should be possible to monitor the rotor axis trajectory in real time during angle-switching NMR experiments, such as dynamic-angle-spinning (DAS) [19–21]. This may require a compromise in the accuracy of the angular measurement, since the time-averaging mode of the voltmeter would have to be temporarily disabled to achieve sufficient time resolution.

Note added in proof

The Lakeshore Hall device HGT-3030 has a specified magnetic sensitivity around 10 times that of the device used for this study, and should provide angle sensitivity approaching 1 millidegree for temperatures between −40 °C and +100 °C.

Acknowledgments

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