Magic angle spinning (MAS) nuclear magnetic resonance (NMR) experiments partially average anisotropic spin interactions in the magnetic resonance Hamiltonian through mechanical rotation of samples about the magic angle (54.7° with respect to the static magnetic field, \( B_0 \)). The spatial averaging extends spin relaxation times and improves the resolution of solid-state NMR spectroscopy (1, 2). Single resonances can often be assigned to chemically distinct nuclear spins to yield site-specific signatures encoding structural information and molecular dynamics (3–7). MAS NMR is, therefore, a powerful technique to characterize diverse molecular architectures including membrane proteins (8–15), amyloid fibrils (16–19), bacterial biofilms (20, 21), and materials and surfaces (22–25).

Mechanical sample rotation must be comparable to, or greater than, the frequency of the internal anisotropic spin interaction to produce significant averaging. Spinning frequencies less than 3 kHz averaged chemical shift anisotropy and weak dipole couplings at the advent of MAS. Currently available spinning frequencies of >150 kHz (26–30) are sufficiently high to attenuate proton homonuclear couplings and yield spectra of solids with resolution approaching that observed in solution-state NMR (26–29). Over the past 60 years of MAS, samples have typically been packed into hollow cylindrical sample containers (rotors), with turbine inserts to supply drive propulsion (Fig. 1A).

The long, narrow cylindrical shape of these rotors and the necessity for them to rotate at the magic angle complicate the sample exchange process. Sample exchanges for cylindrical rotors mandate an angle adjustment of either the rotor or the stator for insertion or ejection within the magnet bore. This alignment typically requires considerable space within the magnet (30). Furthermore, cylindrical rotors for cryogenic MAS dynamic nuclear polarization (DNP) is the technique used in this experiments, aimed at improving NMR signal-to-noise ratio, present significant challenges to microwave coupling into the sample (31–33).

We sought to improve MAS instrumentation to simplify sample exchange, improve DNP, reduce cryogen usage, and access spinning frequencies > 150 kHz (34). Macroscopic metallic spherical rotors have been spun up to 667 kHz using electromagnetic bearings and drive energy (35). Although this technology cannot be directly translated into MAS within superconducting magnets, the fact that macroscopic spheres can be spun effectively is important and exploitable. We therefore turned to spherical rotors for MAS.

Spherical rotors have distinct advantages over cylindrical rotors. Wobbling about the long axis of cylindrical rotors results in bearing collisions that can destroy the sample and stator. The isotropic spherical rotor alleviates these issues, because wobbling about an axis other than the primary spinning axis does not result in stator collisions. Furthermore, our implementation of a spherical rotor enables a simplified vertical sample exchange while providing better access for microwave illumination. Here, we introduce spheres for MAS, demonstrating MAS NMR spectroscopy of samples packed within spherical rotors spinning stably at the magic angle.

### MATERIALS AND METHODS

Commercial sources of relatively low-cost, high-precision spheres are available as industrial lubricants and ball bearings. We machined 36- or 161-μl sample chambers into yttria-stabilized zirconia (ZrO₂) solid spheres with a diameter of 9.525 mm (Fig. 1, B and C). Twelve turbine grooves were cut into the spherical rotor longitudinally (O’Keefe Ceramics). Kel-F spacers and epoxy were used to seal the sample chambers (Fig. 1, B and C). Stators to house the spherical rotors were three-dimensionally (3D) printed from an acrylonitrile-butadiene-styrene material (Form 2 SLA printer, Clear V4 Resin, Formlabs).

All experiments were performed at a \( B_0 = 7.05 \) T corresponding to a \(^{79}\)Br Larmor frequency of 75.214 MHz. Spectra were recorded with a custom-built, two-channel, transmission line probe resonating a split solenoid sample coil. A Bloch decay with a pulse length of
20 μs was used for spherical rotors, with a 1-s recycle delay. Spinning frequencies were measured on a testing apparatus outside the magnet with an LT-880 laser tachometer (Terahertz Technologies Inc.), as shown in fig. S2. Spinning frequencies during the NMR experiments were measured with fiber optics and a MAS control unit (Tecmag).

RESULTS AND DISCUSSION

Spherical rotor design

The spherical rotors contain cylindrical sample chambers and equatorial turbine grooves cut into the surface of the rotor. A large moment of inertia and improved spinning stability are achieved by ensuring that the mass distribution of high-density zirconia is distant from the spinning axis. The 36-μl sample chamber in spherical rotors matches the 3.2-mm cylindrical rotor (Fig. 1, A and B), and we further hollowed out the 9.5-mm–peripheral diameter rotors to accommodate 161 μl of the sample (Fig. 1C). Converting the zirconia rotor body into a turbine, rather than relying on turbine inserts, delivers a robust drive platform with high torque. The combination of cylindrical sample chambers and grooves establishes a preferred axis of rotation about a single axis (Fig. 1, B and C). This allows the spherical rotor to be inserted at arbitrary orientations within the stator (see movie S1). When spinning gas is applied, the sphere quickly samples different orientations until rotation about the preferred axis is established.

Stator for spherical rotor

Prototyping stator geometries with 3D printing greatly accelerated the production of a successful stator design (fig. S1). We chose to use relatively large dimensions (9.5 mm diameter) to leverage rapid prototyping with resolution readily available for 3D printing. For instance, we have now printed and tested 232 stators to spin spherical rotors. We expect improved spinning performance as the fluid flow is further optimized within precision-fabricated stators.

Figure 2 shows a selection of four stator designs that demonstrate progression to the current implementation. Initially, the stator was enclosed, and multiple gas streams (Fig. 2A), comparable to bearings and drive cups within cylindrical MAS stators, were used. However, these designs lead to spinning instability due to poor fluid
flow dynamics. Simplification of the design to a single gas stream resulted in spinning about a single axis. Spinning stability with the single-stream stator was greatly improved by adding a pathway to guide the exhausting gas (Fig. 2B). Positioning the gas inlet aperture within the hemispherical stator at the complement to the magic angle resulted in stable MAS (Fig. 2C). In addition, Fig. 2D shows a vertical extrusion of 2 mm that improves fluid flow, resulting in faster spinning. Blind holes for fiber optics pass sufficient light to enable spinning frequency detection without affecting fluid flow (Fig. 2D).

Our current stator design (Figs. 2D and 3) incorporates only a single gas stream, which simultaneously provides bearing gas to reduce friction, propulsion to generate and maintain angular momentum, and variable temperature control for thermostating. Introducing this gas stream under the sphere $35.3^\circ$ off of $B_0$ suspends the sphere and generates rotation of the sample at the magic angle of $54.7^\circ$ (Fig. 3A). A plane at the end of the gas inlet, which is tangent to the hemispherical drive cup, guides the spinning gas into the stator (Fig. 3B). The spinning gas then exits through the exhaust opposite of the gas inlet. The gas inlet and exhaust are designed in a common plane that is perpendicular to the spinning axis of the rotor. Figure 3 (C and D) shows the flow path of the spinning gas through the stator.

### NMR probes

The transmit-receive coil is a four-turn split solenoid wrapped around the stator. This design allows vertical access to the sample, albeit with decreased NMR sensitivity due to a low filling factor. We designed stators that were compatible with our current NMR probes. The design interfaces to an adjustment apparatus for magic angle optimization and also improves microwave illumination for DNP (Fig. 4). Implementation of spherical rotors simplified sample exchange by allowing vertical access to the sample. This eliminated the need for rotation of either the rotor or the stator before sample exchange, as is necessary for cylindrical rotors (30). The sample exchange now mimics systems typically used in solution NMR instrumentation. A simple tube connected to a wet/dry vacuum (model 3VE20, Dayton Electric Mfg. Co.) was used to extract and insert the sphere. With minor adjustments, this new compact MAS NMR stator and rotor design could be implemented in a wide variety of NMR probes for both narrow and wide bore magnets.

### Results with KBr

$^{79}$Br yields quadrupolar spinning sidebands that are used to optimize the magic angle (36). Rotational echoes were observed at 10 ms in the time domain (Fig. 5A). The Fourier transform of the signal showed sidebands separated by the spinning frequency of 4297 Hz (Fig. 5B). The central resonance had a width of 123 Hz at half height, while the first sideband had a width of 143 Hz at half height, indicating spinning closely matching to $54.7^\circ$ off the $B_0$ magnetic field. Figure 5C shows peak height ratios of the center band and second sidebands versus deviation from the magic angle, similar to the description by Frye and Maciel (36). The relative height of the center band compared to the sidebands decreases as the angle of rotation approaches the magic angle. Figure 5C indicates the ability to optimize the magic angle in MAS NMR experiments. Figure 5 (D and E) shows the regulated and unregulated spinning frequency over 22 min. Regulation of spinning frequency used a 12-ohm nichrome wire
Fig. 3. Our current stator design with a single gas stream. (A) The gas introduced under the sphere 35.3° off of $B_0$ suspends the sphere and aligns its spinning axis with the magic angle. (B) A section view from (A) shows the gas inlet path and how the gas is directed into the drive cup by a tangent plane. (C and D) Overall flow path of the spinning gas from two separate isometric views.

Fig. 4. Implementation of rotating spheres into a transmission line probe previously used in cryogenic MAS-DNP. (A) The pivots of the 3D printed stator serve as the gas inlet and as the pivot point for the magic angle adjustment. The complete NMR probe head includes fiber optics for spinning frequency detection, magic angle adjustment via a threaded adjustment assembly, waveguide to transmit microwaves to the sample for DNP, tube for sample exchange, and a 3D printed post for connection of the stator to the gas supply. An isometric view (B) and a section view (C) show the path for the introduction of microwaves to the sample for DNP. RF, radio frequency.
heating element to regulate the gas temperature (fig. S2) \((37)\). Figure 5F indicates that 98% of the frequencies measured fall within 4560 ± 1 Hz. This frequency regulation system, which improves spinning stability in the spheres, has yet to be implemented with NMR signal detection.

The first-order sidebands in \(^{79}\)Br spectra of KBr were used to compare NMR sensitivity of three MAS rotor geometries: a 3.2-mm cylindrical rotor, a 36-μl spherical rotor, and a 161-μl spherical rotor (Fig. 1, D to F). Each spectrum is an average of 256 transients. Although the filling factor of the spherical rotors in a split solenoid coil is not ideal, the 161-μl spherical rotor yields better signal-to-noise ratios than the 3.2-mm cylindrical rotor.

We also investigated mechanical advantages imparted by the spherical shape of the rotors through further increasing centrifugal forces from spinning. Helium gas at high pressure resulted in >10-kHz spinning of the 9.5-mm-diameter spherical rotors. Rotors within the stator design shown in Figs. 2D and 3 were spun to 10.6 kHz using 11-bar He\((g)\) on a testing apparatus outside the magnet (fig. S3). The sphere maintained spinning stability above 10 kHz, similar to that demonstrated in Fig. 5D. This observation provides promise

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**Fig. 5. Magic angle adjustment and spinning stability regulation of MAS with spherical rotors.** \(^{79}\)Br magnetic resonance of MAS spheres packed with KBr. (A) Free induction decay of 64 transients with rotational echoes observed out to 10 ms. (B) Spinning sidebands in the frequency domain indicate spinning of 4.3 kHz stably at the magic angle. (C) Optimization of the magic angle at a spinning frequency of 2.5 kHz. The height ratio \((R)\) of the center band peak relative to the second sideband decreases as the angle of rotation approaches 54.7° from \(B_0\) \((36)\). (D) Spinning frequency stability over 22 min with and without spinning regulation controlled through a resistive heating element circuit. (E) Expansion of spinning frequency shows moderate excursion in spinning frequency of less than 20 Hz without regulation and improved frequency stability with regulation. (F) Histogram of spinning frequencies showing the rotor spinning at 4560 ± 1 Hz for 98% of the 22 min observed. a.u., arbitrary units.
CONCLUSION AND OUTLOOK

MAS spheres have been demonstrated with practical advantages over their cylindrical counterparts. Future implementation of spherical rotors is expected to lead to higher spinning frequencies through the optimization of turbine and stator geometry. With the relatively straightforward design of the current spherical rotors and supporting stators, the implementation of MAS spheres described here should scale well to micrometer-sized rotors. Access to small rotors will better enable MAS at frequencies >150 kHz (34), and we are currently designing spheres ≤2 mm for MAS DNP.

The single aperture in stators used to spin spherical rotors could facilitate adoption of cryogenic MAS DNP into narrow-bore magnets. Currently, vacuum-jacketed transfer lines are required to provide separate bearing, drive, and variable temperature gases. MAS spheres, as demonstrated herein, only require a single gas stream, decreasing the space required within high-field superconducting magnet bores.

NMR sensitivity of samples packed within spherical rotors will be improved through modifications of the transmit-receive coil and stators. For instance, coil geometries such as saddle coils will yield better filling factors and are still amenable to simplified vertical sample exchange. Such inductors will also permit more efficient microwave coupling to the sample for MAS DNP experiments while maintaining sample exchange ability.

Finally, spherical rotors for magnetic resonance could also have widespread application in switched angle spinning (SAS) (38–40) and double angle rotation (DOR) (41, 42). For instance, introducing a second gas inlet into the stator could establish spinning off of the magic angle. Spherical rotors are expected to play a prominent role in the future development of MAS NMR.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/9/eaau1540/DC1

REFERENCES AND NOTES


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Magic angle spinning spheres
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Sci Adv 4 (9), eaau1540.
DOI: 10.1126/sciadv.aau1540