Probing Mg-ion Transport in Antiperovskites via Ultrahigh Field ^{25}Mg NMR

David M. Halat[1,2,3], Haoyu Liu[4], Kwangnam Kim[5,6], Grant C. B. Alexander[7], Xiaoling Wang[8,9], Amrit Venkatesh[8], Adam R. Altenhof[10], Harris E. Mason[11], Saul H. Lapidus[12], Jeong Seop Yoon[13], Ivan Hung[8], Zhehong Gan[8], Jordi Cabana[7,14], Donald J. Siegel[13], Jeffrey A. Reimer[2,3], Baris Key[4]

1. Colorado School of Mines; 2. University of California Berkeley; 3. Lawrence Berkeley National Laboratory; 4. Argonne National Laboratory; 5. University of Michigan; 6. Lawrence Livermore National Laboratory; 7. University of Illinois at Chicago; 8. National High Magnetic Field Laboratory, Florida State University; 9. California State University East Bay; 10. Los Alamos National Laboratory (MPA-Q); 11. Los Alamos National Laboratory (Chemistry Division); 12. Advanced Photon Source, Argonne National Laboratory; 13. University of Texas at Austin; 14. Argonne National Laboratory (Materials Science Division)

Funding grants: D.M.H., J.C., D.J.S., J.A.R., B.K. (DOE BES JCESR, DE-AC02-06CH11357); X.W., A.V., I.H., Z.G. (NSF DMR-2128556, NSF DMR-1039938, NSF DMR-0603042, NIH BTRR 1P41 GM122698); K.K. (DOE DE-AC52-07NA27344); X.W. (DOE DE-SC0025712); D.M.H. (Pines Magnetic Resonance Center Fellowship); J.C., D.J.S., J.A.R., B.K. (DOE Office of Science, Argonne National Laboratory, DE-AC02-06CH11357); D.J.S., J.A.R., B.K. (DOE, Los Alamos National Laboratory, 89233218CNA000001).

Magnesium-ion batteries promise safer, higher-capacity energy storage than lithium-ion systems, but development has been hindered by the absence of solid electrolytes capable of fast Mg-ion conduction. **Antiperovskite** materials such as Mg_3AsN and Mg_3SbN have been proposed as candidates, yet their ion transport properties have not been experimentally verified.

To address this challenge, we performed natural-abundance ^{25}Mg solid-state NMR at 35.2 T using the MagLab's **36 T Series-Connected Hybrid (36T SCH) magnet**, the highest-field NMR instrument in the world. The ultrahigh field dramatically reduces pattern broadening arising from the second-order quadrupolar interaction, enabling acquisition of complete, ultra-wideline ^{25}Mg spectra in just **20 minutes**. At conventional fields (*e.g.*, 11.7 T), the same measurements require "piecewise" acquisition **over nearly two weeks**. This gain in efficiency made variable-temperature experiments practical, allowing us to quantify Mg-ion hopping rates and activation energies directly. The 36T SCH therefore enables ^{25}Mg NMR experiments that would otherwise be impractical, reducing weeks of effort to less than an hour!

These studies reveal the largest quadrupolar coupling constants reported for magnesium to date (up to 22 MHz) and provide direct evidence of fast, low-barrier Mg-ion motion in antiperovskites. By confirming the predicted ion transport mechanisms, this work advances the atomic-scale understanding of these materials and supports the **rational design of new solid electrolytes for next-generation, beyond-lithium battery technologies**.

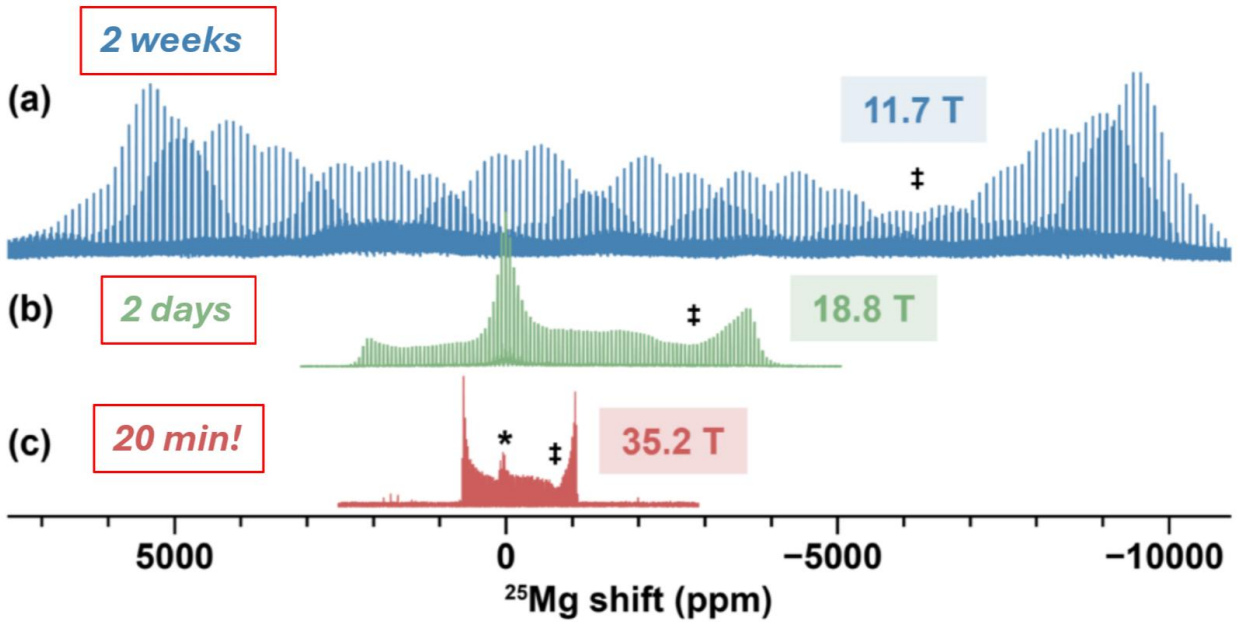

Figure: Variable-field ^{25}Mg static QCPMG spectra of Mg_3AsN acquired at (a) 11.7 T, (b) 18.8 T, and (c) 35.2 T (using the 36T SCH). Acquisition times were approximately 2 weeks, 2 days, and 20 min, respectively. *Mg_3As_2 impurity. ‡Depletion of signal due to overlap of central transition (CT) and satellite transition (ST) patterns.

Facilities and instrumentation used: Solid-State NMR Facility: **36 T/40 mm Series Connected Hybrid Magnet** (35.2 T/1.5 GHz) and **18.8 T/63 mm/800 MHz** solid-state NMR spectrometer (800#1)

Citation: Halat, D.M.; Liu, H.; Kim, K.; Alexander, G.C.; Wang, X.; Venkatesh, A.; Altenhof, A.R.; Mason, H.E.; Lapidus, S.H.; Yoon, J.; Hung, I.; Gan, Z.; Cabana, J.; Siegel, D.J.; Reimer, J.A.; Key, B., *Mg-Ion Conduction in Antiperovskite Solid Electrolytes Revealed by 25Mg Ultrahigh Field NMR and First-Principles Calculations,* **Journal of the American Chemical Society**, **147** (31), 27949–27961 (2025) **doi.org/10.1021/jacs.5c07442**