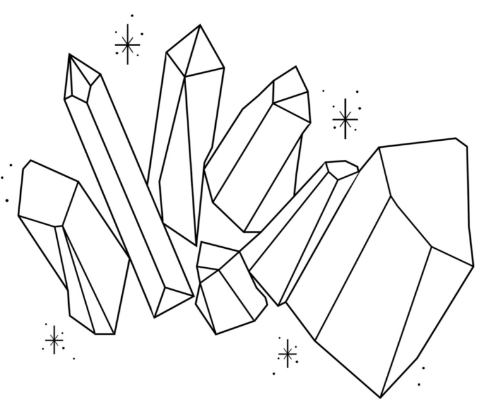
# Dynamics of $^8$Li$^+$ Ions Implanted in α-Quartz

W. Andrew MacFarlane,[1, 2, 3] Ryan M. L. McFadden,[1, 2] John O. Ticknor,[1, 2] Aris Chatzichristos,[2, 4] David L. Cortie,[1], Martin H. Dehn,[2, 4] Sarah R. Dunsiger,[3] Derek Fujimoto,[2, 4] Zeehoon Jang,[3] Victoria L. Karner,[1, 2] Robert F. Kiefl,[4, 2, 3] Philip Macau,[1, 2] Gerald D. Morris,[3] Signy Spencer,[1, 2] and Monika Stachura [3, 5]

[1]Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada, [2]Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver, BC V6T 1Z4, Canada, [3]TRIUMF, Vancouver, BC V6T 2A3, Canada, [4]Department of Physics, University of British Columbia, Vancouver, BC V6T 1Z1, Canada, [5]Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

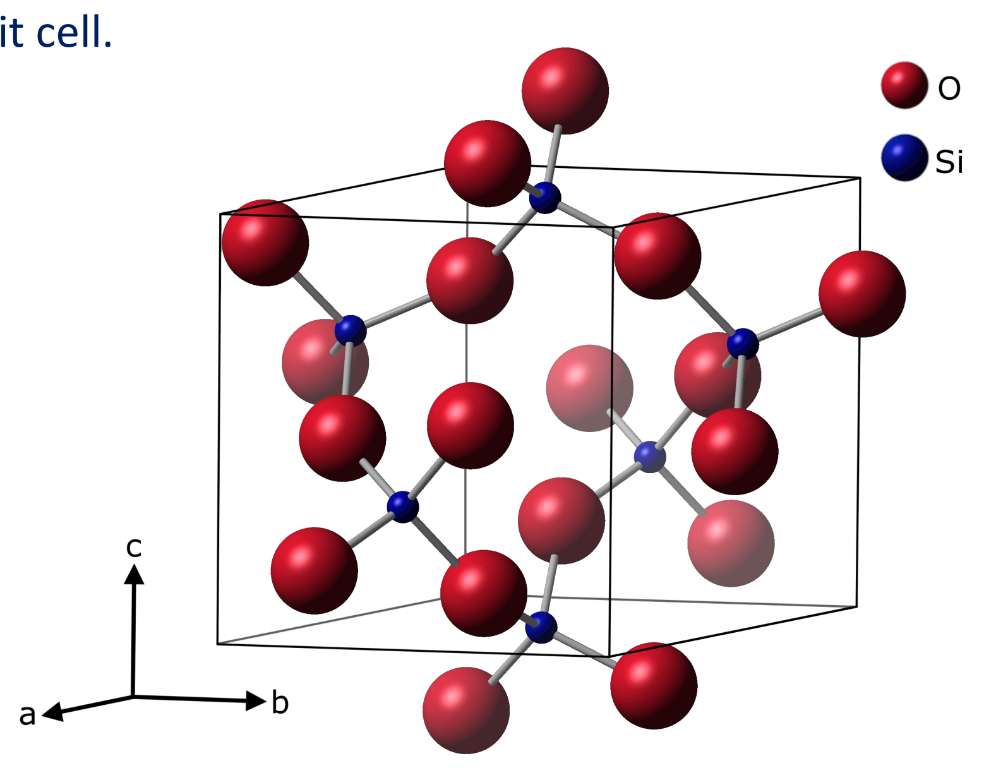
## Introduction to the Study

- Quartz, α-$SiO_2$, a common oxide insulator, has important applications based on its piezoelectric properties.
- Applications include the development of novel battery materials, improvement of ultrasonic transducers or chemical sensors.
- Here, we study the site and dynamics of isolated implanted $^8$Li$^+$ ions in an artificial quartz crystal.
- $^8$Li$^+$, a radioactive isotope made of 3 protons and 5 neutrons, is used in this ß-NMR experiment as a probe as it is the longest-lived unstable isotope of lithium with a half-life of 0.848 s.
- Monitoring the asymmetry of $^8$Li$^+$'s parity violating beta-decay as a function of temperature, one can measure the nuclear magnetic resonance of the implanted ion and its spin-lattice relaxation.
- Conclusions can then be made upon structure and function of the ion's diffusion.
- We find remarkably fast spin relaxation with a strong temperature dependence below 300 K which may be due to surprisingly fast diffusion at low temperatures.



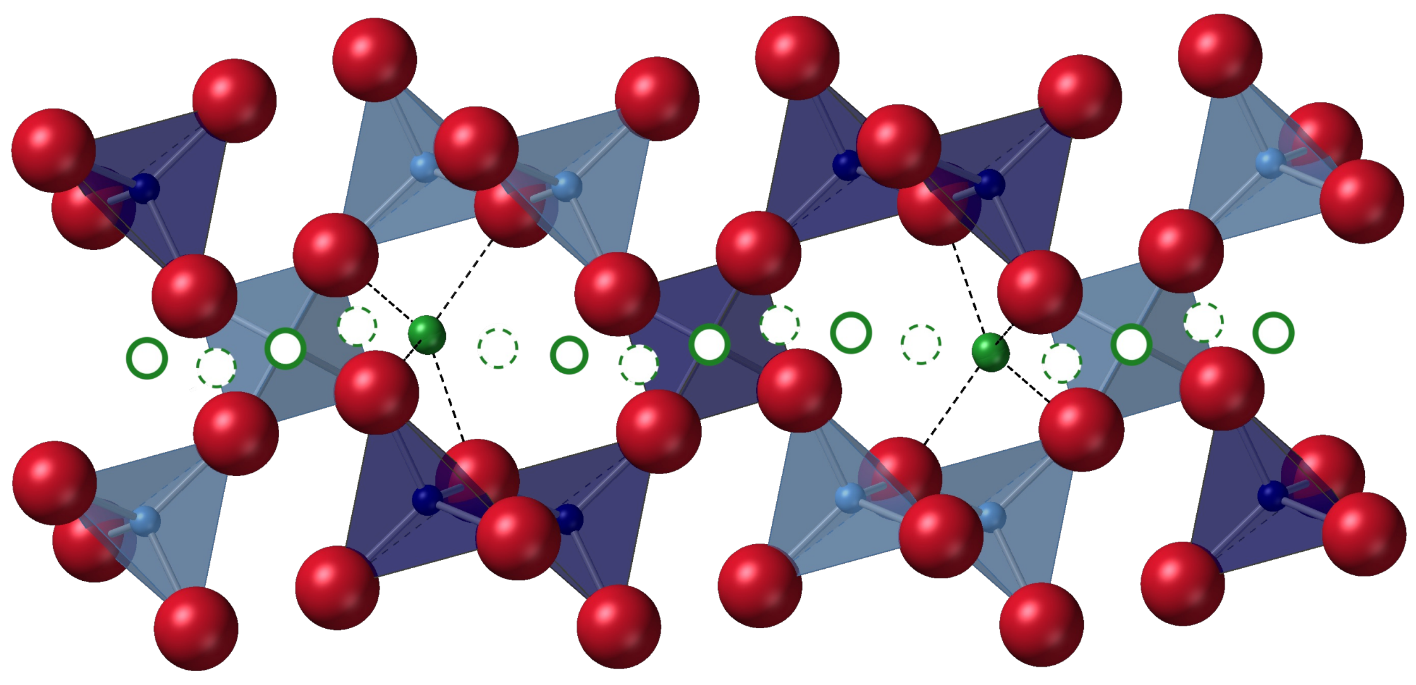
## α-Quartz on a Microscopic Level

- Quartz is a low energy, relatively low symmetry crystal comprised of a 3D network of silicon-oxygen tetrahedrons forming a crystal lattice.
- The tetrahedrons are corner-shared, linked together by oxygens.
- There are two long silicon-oxygen polar covalent bonds and two shorter ones.
- There are 3 formula units of $SiO_2$ within the trapezoidal unit cell.



- The full crystal structure is a repetition of the unit cell.
- The point group is $P3_221$ or $P3_121$ depending on the handedness.

## $^8$Li$^+$ Mechanism of Diffusion



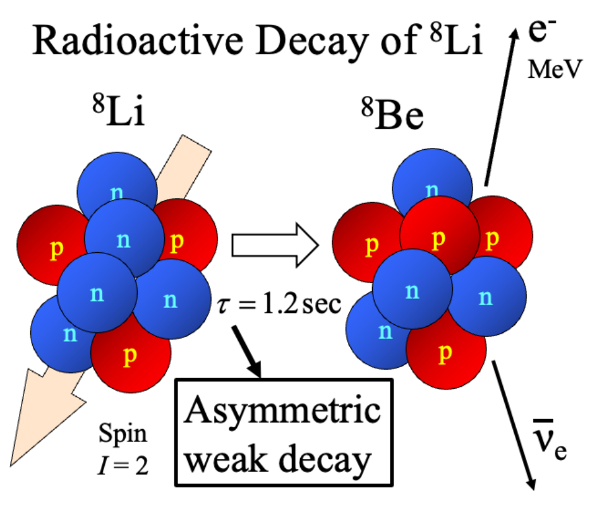
● Occupied low potential energy site

○ Unoccupied low potential energy site

◌ Barrier site

## Technique of ß-NMR

- A highly spin polarized beam of our isotope, $^8$Li$^+$, is directed to an 8X10 mm sample of artificially grown quartz.
- After implantation of $^8$Li$^+$, the isotope stops in the lowest potential energy site and potentially diffuses through the sample if the temperature and material permits.
- A radioactive weak, parity violating, beta decay follows.

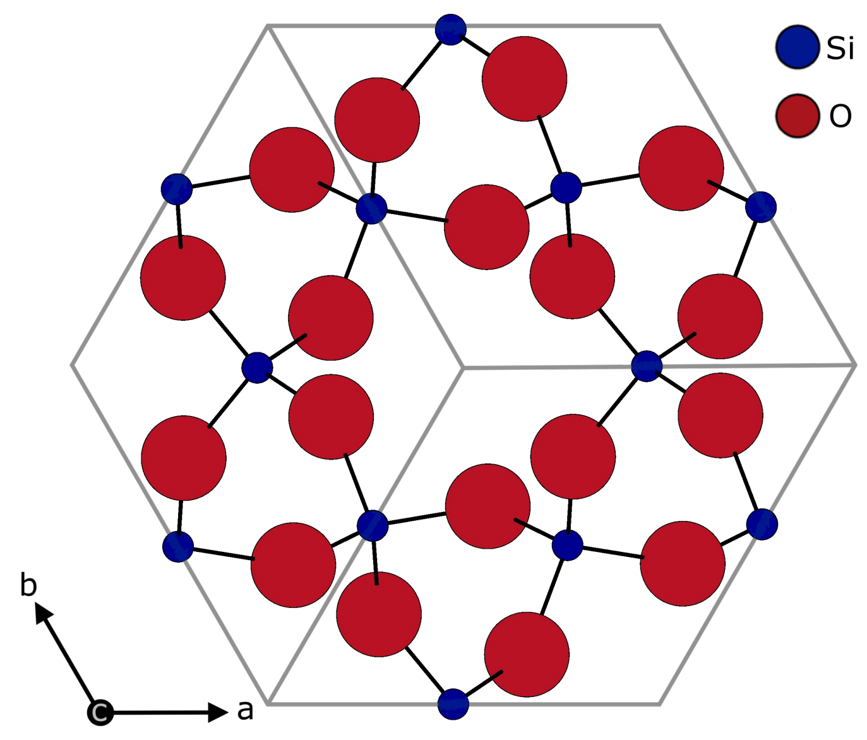


$$A(t) = \frac{N_F(t) - N_B(t)}{N_F(t) + N_B(t)}$$

- A signal is given from the high energy electrons emitted hitting the forward and backward scintillation detectors in a spectrometer.
- This tells us about the spin relaxation of $^8$Li$^+$ and thus the local magnetic and electronic environment of the material.

## C-Axis Channel in α-Quartz

- The twisting and turning of the silicon-oxygen tetrahedrons create helical channels parallel to the c-axis.
- The large centre channel in this figure is thought to be the only one that can comfortably accommodate guest ions in quartz.

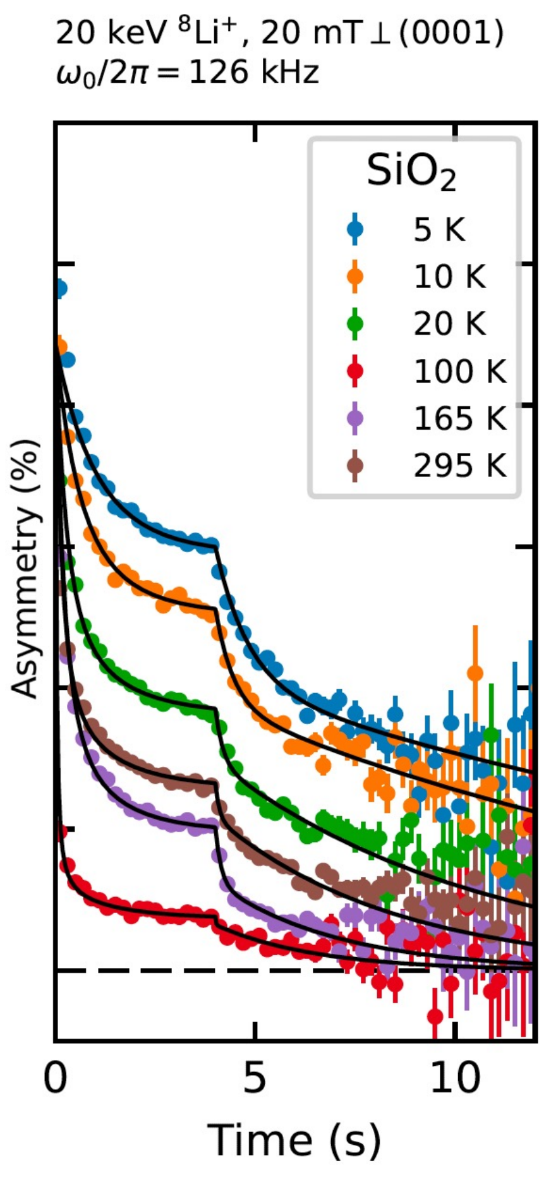


- Our goal of this study is to elucidate fundamental aspects of the mobility of lithium ions in the dilute limit of α-quartz.
- $^8$Li$^+$'s diffusion in the c-axis channel is confined to 1D and is anisotropic.
- We may find impurities that replace the Si atoms in the quartz structure such as H or Al.

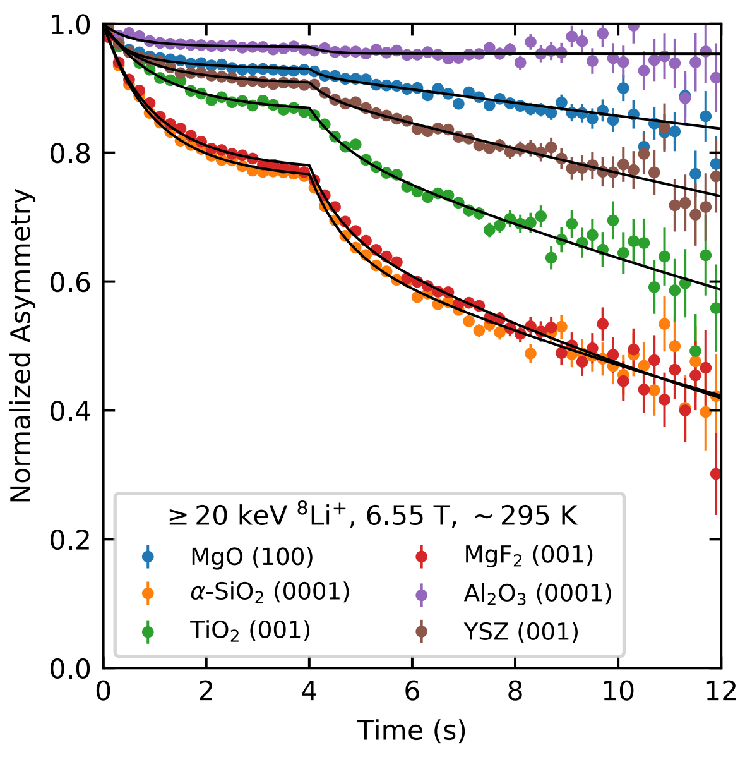
## Current Inquiries

- Looking forward, we seek to understand unexplained trends in our data.
- The peak of the lithium's diffusive mobility and thus the fastest spin relaxation occurs at 100 K,
a highly unexpected result as this is far below room temperature.
- Another observation in the data is that there appears to be two speeds of diffusion which is quite perplexing.
- A potential explanation includes relating the fast component to the formation of Li$^0$ which is a neutral
Li atom that would be present in the quartz lattice instead of the expected $^8$Li$^+$.
- The Li$^0$ contains an unpaired electron which produces a large magnetic field on the Li nucleus.

## $^8$Li$^+$ ß-NMR Data



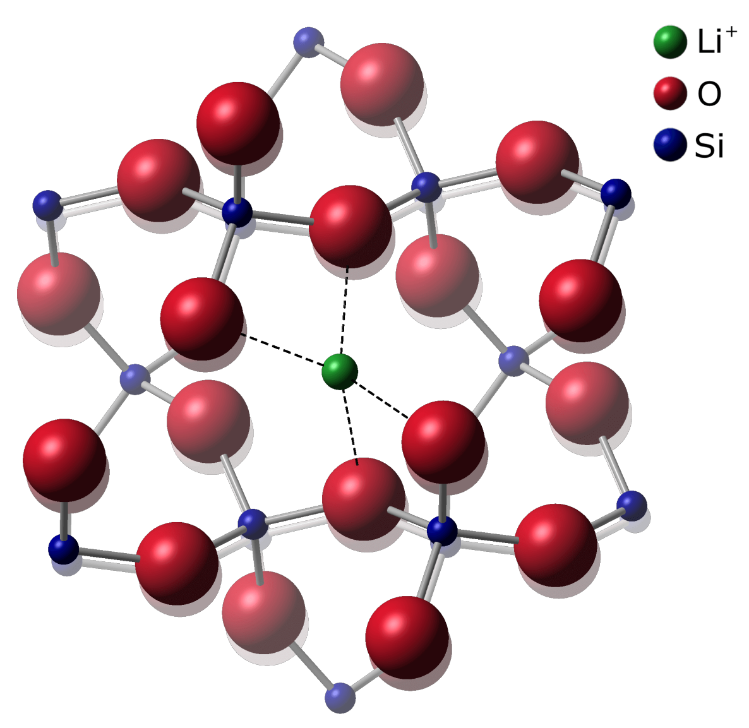
- The relationship between spin relaxation and temperature in quartz.



- The spin relaxation data for an array of oxide insulators.

## Proposal of $^8$Li$^+$ Site in α-Quartz

- *Where is the lithium ion's lowest potential energy site situated?*
- If $^8$Li$^+$'s nearby atoms are repelling it, the energy cost will be too great and it will migrate to a lower energy site.
- It is hypothesized that $^8$Li$^+$ will sit in a 4-fold coordinated state within the large c-axis channel bound to the 4 nearest oxygen atoms.



- There are three 2-fold axes located a third apart running through the silicon atoms across the channel from one another.
- We propose there is one lithium site per two-fold axis, located a 1/3 of a c-axis lattice constant away from each other within the c-axis channel. This indicates there are 3 sites per unit cell.

## References

Botis, S.M., Pan, Y. Theoretical calculations of [AlO4/M+]0 defects in quartz and crystal-chemical controls on the uptake of Al. *Mineral. Mag.* 2009, *73* (4), 537–550. https://doi.org/10.1180/minmag.2009.073.4.537

Brice, J.C. Crystals for Quartz Resonators. *Rev. Mod. Phys.* 1985, *57* (1), 105–146. https://doi.org/10.1103/revmodphys.57.105

Donnay, H., Y. Le Page. The Vicissitudes of the Low-Quartz Crystal Setting or the Pitfalls of Enantiomorphism. *Acta Cryst.* 1978, *34* (4), 584–594. https://doi.org/10.1107/s0567739478001242

Follstaedt, D.M., Richards, P. M. NMR Relaxation in the Superionic Conductor β-LiAlSiO4. *Phys. Rev. Lett.* 1976, *37* (23), 1571–1574. https://doi.org/10.1103/physrevlett.37.1571

Glazer, A. M. Confusion over the Description of the Quartz Structure yet Again. *J. Appl. Crystallogr.* 2018, *51* (3), 915–918. https://doi.org/10.1107/s160057671800434x

Hughes, R. C. Electronic and Ionic Charge Carriers in Irradiated Single Crystal and Fused Quartz. *Radiat. Eff. Defects Solids.* 1975, *26* (4), 225–235. https://doi.org/10.1080/00337577508232996

Jain, H., Nowick, A. S. Radiation-Induced Conductivity in Quartz Crystals. *J. Appl. Phys.* 1982, *53* (1), 485–489. https://doi.org/10.1063/1.329950

MacFarlane, W.A., McFadden R.M.L. ß-NMR Studies of Lithium-Ion Mobility in Tunnel Structured Materials TRIUMF ECC Original Proposal of M1771. 2017.

MacFarlane, W.A., McFadden R.M.L. ß-NMR Studies of Lithium-Ion Mobility in Tunnel Structured Materials TRIUMF ECC Progress Report of M1771. 2018.

Morris, G. D. β-NMR. *Hyperfine Interact.* 2013, *225* (1-3), 173–182. https://doi.org/10.1007/s10751-013-0894-6

Ostadhossein, A., Kim, S., Cubuk, E. D., Qi, Y. van Duin, A. C. T. Atomic Insight into the Lithium Storage and Diffusion Mechanism of $SiO_2/al_2O_3$ Electrodes of Lithium Ion Batteries: ReaxFF Reactive Force Field Modeling. *J. Phys.Chem*. 2016, *120* (13), 2114–2127. https://doi.org/10.1021/acs.jpca.5b11908

Plata, J., Breton, J., Girardet, C. Theoretical model for the electrodiffusion of M+ (M =Li, Na, K) ions in a quartz crystal. Phys. Rev. B: Condens. Matter. 1988, *38* (5), 3482–3493. https://doi.org/10.1103/physrevb.38.3482

Shannon, R. D., Prewitt, C. T. Effective Ionic Radii in Oxides and Fluorides. *Acta Crystallogr., Sect. B: Struct. Sci.* 1969, *25* (5), 925–946. https://doi.org/10.1107/s0567740869003220

Snow, E. H., Gibbs, P. Dielectric Loss due to Impurity Cation Migration in α-Quartz. *J. Appl. Phys.* 1964, *35* (8), 2368–2374. https://doi.org/10.1063/1.1702865

Verhoogen, J. Ionic Diffusion and Electrical Conductivity in Quartz. *Am Min.* 1952, *37*, 637–655.

Voss, A., Pearson, Billowes, M. R. J., Buchinger, F., Chow, K. H., Crawford, J. E., Hossein, M., Kiefl, R. F., Levy, C. D. P., MacFarlane, W. A., Mané, E., Morris, G. D., Parolin, T. J., Saadaoui H., Salman, Z., Smadella, M., Song, Q., Wang, D. The Development of Pure β-NQR Techniques for Measurements of Nuclear Ground State Quadrupole Moments in Lithium Isotopes. *J. Phys. Conf. Ser.* 2011, *312* (9), 092063–092063. https://doi.org/10.1088/1742-6596/312/9/092063

Weil, J. V. A Review of Electron Spin Spectroscopy and Its Application to the Study of Paramagnetic Defects in Crystalline Quartz. *Phys. Chem. Miner.* 1984, *10* (4), 149–165. https://doi.org/10.1007/bf00311472

## Acknowledgements

- Thank you to TRIUMF CMMS and ISAC facility staff for technical support.
- UBC Work-Learn program for the undergraduate research position funding.

TRIUMF

Stewart Blusson
Quantum Matter Institute

UBC
THE UNIVERSITY
OF BRITISH COLUMBIA