

Supporting Information for

'Evaluating Lithium Diffusion Mechanisms in the Complex Spinel $\text{Li}_2\text{NiGe}_3\text{O}_8$ '

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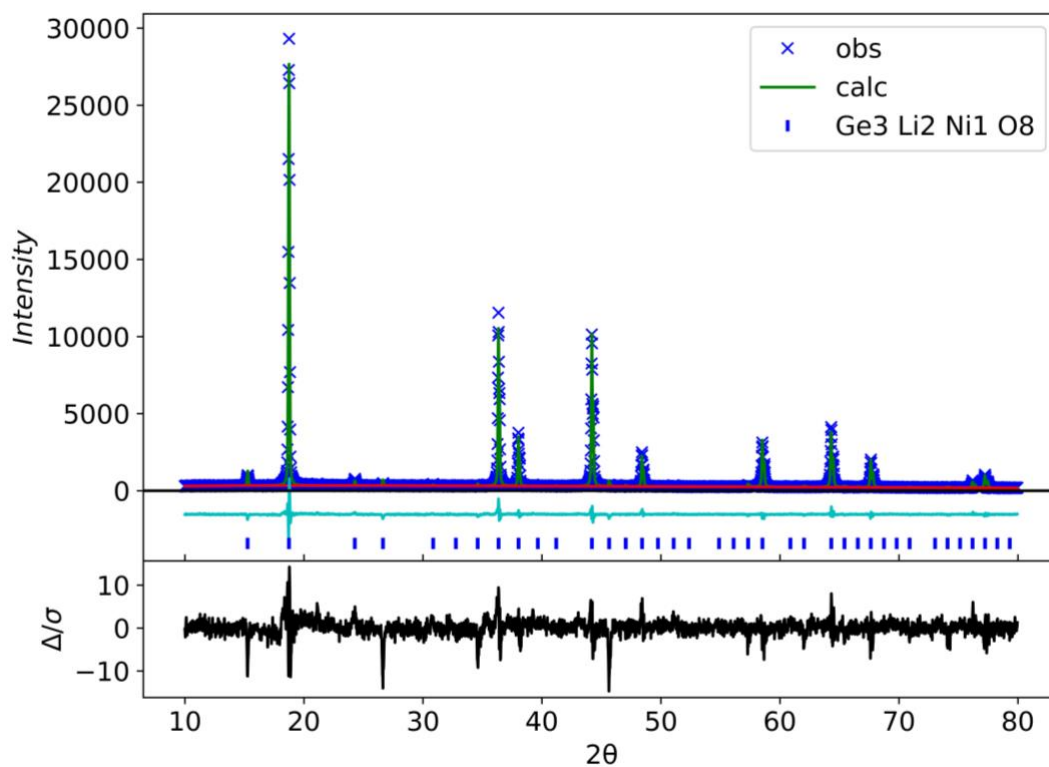


Figure S1: Rietveld refinement of the room temperature XRD data for $\text{Li}_2\text{NiGe}_3\text{O}_8$ after calcination. All corresponding parameters are given in Table S1.

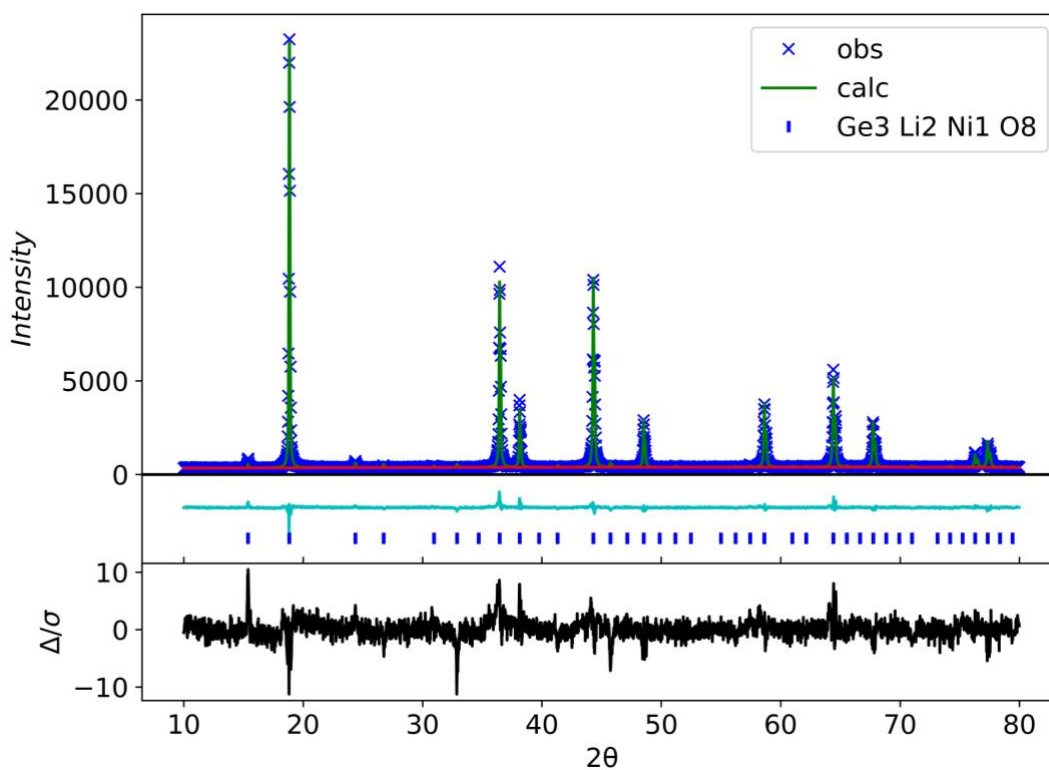


Figure S2: Rietveld refinement of the room temperature XRD data for $\text{Li}_2\text{NiGe}_3\text{O}_8$ after sintering for 6 hours at 1223 K. All corresponding parameters are given in Table S1.

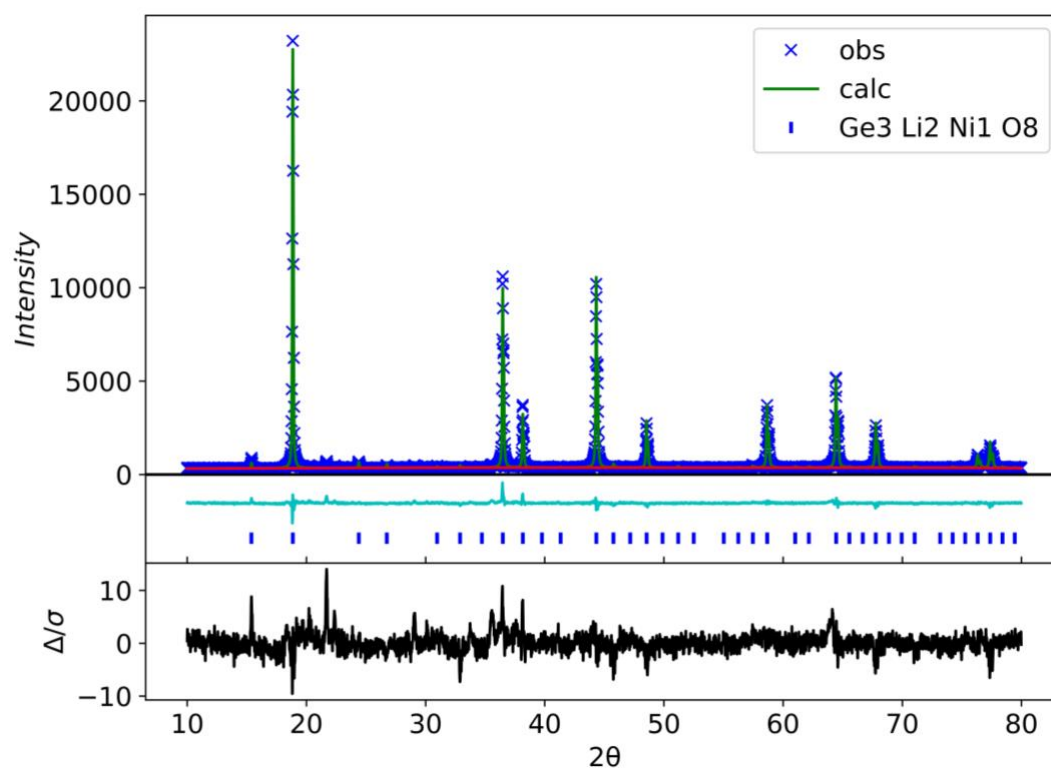


Figure S3: Rietveld refinement of the room temperature XRD data for $\text{Li}_2\text{NiGe}_3\text{O}_8$ after sintering for 24 hours at 1223 K. All corresponding parameters are given in Table S1.

Table S1: Refined structural parameters for $\text{Li}_2\text{NiGe}_3\text{O}_8$ at room temperature for the calcined and sintered (6 and 24 h) samples.

		Powder	6 h	24 h
Cell	$a / \text{\AA}$	8.18479 (5)	8.18335 (5)	8.18026 (5)
	$V / \text{\AA}^3$	548.306 (11)	548.016 (9)	547.395 (9)
Statistics	wR	8.95%	6.77%	7.57%
	χ^2	1.87	1.59	1.72
Li	$x = y = z$	0.018	0.018	0.018
	Occupancy	1.0	1.0	1.0
	$U_{\text{iso}} / \text{\AA}^2$	0.05	0.05	0.05
Ni	$x = y = z$	0.625	0.625	0.625
	Occupancy	1.0	1.0	1.0
	$U_{\text{iso}} / \text{\AA}^2$	0.0373 (29)	0.0301 (31)	0.0286 (31)
Ge	x	0.125	0.125	0.125
	y	0.3779 (2)	0.3758 (1)	0.3750 (2)
	z	0.8722 (2)	0.8742 (1)	0.8750 (2)
	Occupancy	1.0	1.0	1.0
	$U_{\text{iso}} / \text{\AA}^2$	0.0594 (8)	0.0240 (6)	0.0200 (7)
O1	$x = y = z$	0.3759 (13)	0.3653 (10)	0.3714 (10)
	Occupancy	1.0	1.0	1.0
	$U_{\text{iso}} / \text{\AA}^2$	0.1790 (48)	0.0993 (42)	0.0573 (35)
O2	x	0.0930 (3)	0.0924 (3)	0.0932 (3)
	y	0.1344 (5)	0.1215 (4)	0.1265 (5)
	z	0.4046 (5)	0.3893(5)	0.3913 (5)
	Occupancy	1.0	1.0	1.0
	$U_{\text{iso}} / \text{\AA}^2$	0.0150 (9)	0.0098 (8)	0.0121 (9)

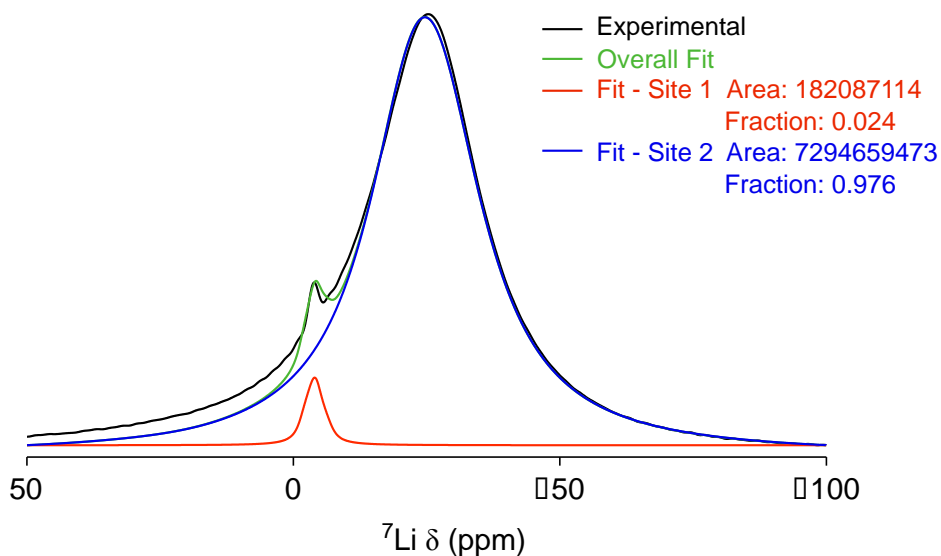


Figure S4: Simulation of the ${}^7\text{Li}$ MAS NMR spectrum obtained at 60 kHz (shown as an inset in Figure 3(a) in the main manuscript). The spectrum was fitted to determine the ratio of Li species on the octahedral $12d$ and tetrahedral $8c$ sites. The fit of the $12d$ site is shown in red and the $8c$ site is shown in blue, with fractions of 0.024 and 0.976, respectively.

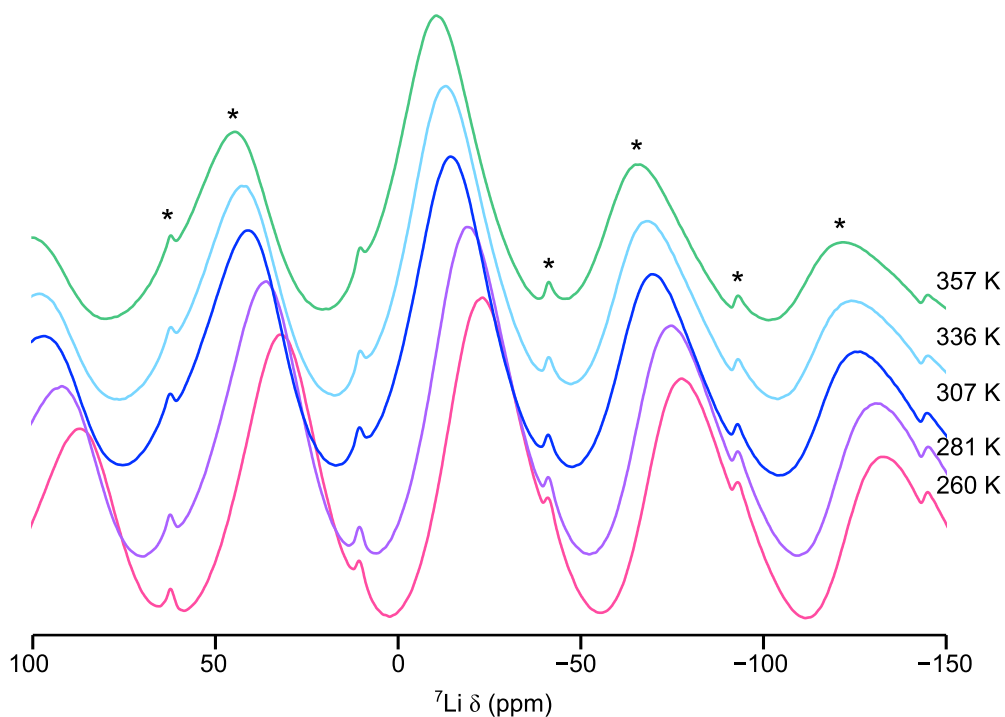


Figure S5: VT ${}^7\text{Li}$ MAS NMR spectra for $\text{Li}_2\text{NiGe}_3\text{O}_8$ obtained over the temperature range 260 – 357 K. The MAS rate was 10 KHz.

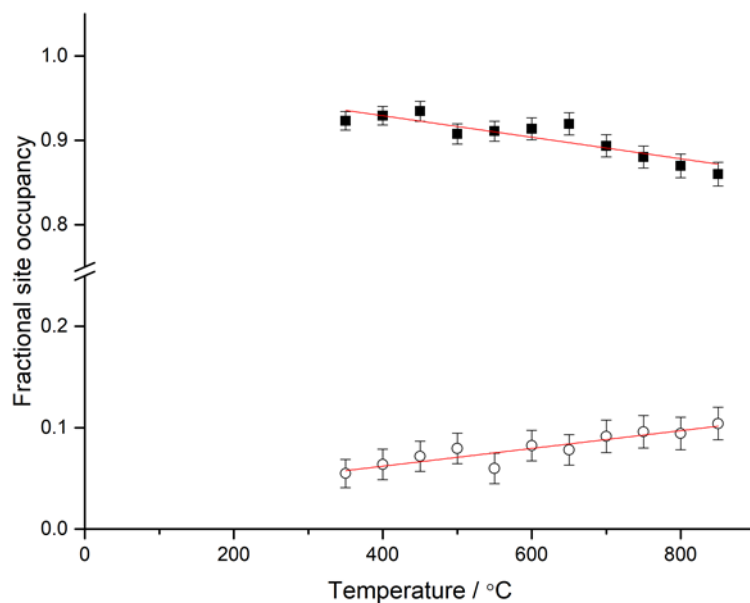


Figure S6: Variation in the fractional site occupancies of the 8c (squares) and 12d (circles) Li sites in $\text{Li}_2\text{NiGe}_3\text{O}_8$ with increasing temperature. Values were previously calculated from neutron diffraction data by Reeves-McLaren *et al.*⁴ Occupancies of 0.97 and 0.03 for the 8c and 12d sites, respectively, were calculated via extrapolation (red lines) of the high temperature data.

Table S2: Summary of parameters used to calculate of the diffusion coefficient for Li-ions in $\text{Li}_2\text{NiGe}_3\text{O}_8$, obtained from Rietveld refinements of the neutron diffraction data.

	Hopping Pathway	N_i	$Z_{v,i}$	S_i (cm)	D_{Li} ($\text{cm}^2 \text{s}^{-1}$)
D_{Li1}	8c to 12d	3	0.97	2.95×10^{-8}	3.72×10^{-12}
D_{Li2}	12d to 8c	2	0.03	2.95×10^{-8}	1.69×10^{-13}
Total D_{Li} (300K) = $3.89 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$					

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