Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Ordering by substitution: the case of $Na_{2-x}Li_xGa_7$

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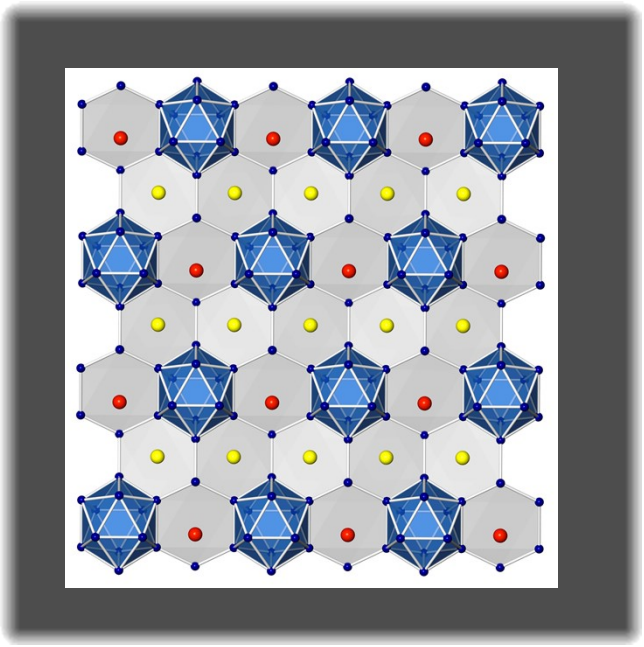

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Table S1 Crystallographic data for $NaLiGa_7$.

Composition	$NaLiGa_7$
Molar mass / g mol^{-1}	517.991
Crystal system; space group	orthorhombic, *Cmce* (no. 64)
a / Å	8.562(1)
b / Å	14.822(2)
c / Å	11.454(2)
V / Å^3	1453.6(4)
Z; ρ_{calc} / g cm^{-3}	8; 4.719
Diffractometer	Rigaku AFC7, Saturn 724+CCD detector
λ / Å	0.71073 (Mo*K*α)
Temperature / K	293
Crystal shape	irregular
Crystal size / mm	0.12 × 0.08 × 0.06
μ / mm^{-1}	25.51
Absorption correction	multi-scan
θ range / deg.	2.75–37.00
Indexes ranges	$-14 \le h \le 12$, $-23 \le k \le 25$, $-10 \le l \le 19$
F(000) / e	1848
Independent reflections	1949
Reflections $F_o > 4\sigma F$	1760
Parameters refined	49
GooF	1.123
R_1, $F_o > 4\sigma F_o$	0.0343
R_1, all data	0.0414

Table S2 Atomic coordinates and displacement parameters (in Å^2) for $NaLiGa_7$.

Atom	Site	Occupancy	*x / a*	*y / b*	*z / c*	U_{eq}/U_{iso}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga1	8*f*	1	0	0.10624(5)	0.81844(7)	0.0133(2)	0.0166(3)	0.0113(3)	0.0119(3)	0	0	0.0018(2)
Ga2	8*f*	1	0	0.17692(5)	0.04241(7)	0.0132(2)	0.0169(3)	0.0075(2)	0.0151(3)	0	0	–0.0016(2)
Ga3	16*g*	1	0.15421(6)	0.05125(3)	0.16733(4)	0.0118(1)	0.0145(2)	0.0104(2)	0.0105(2)	–0.0001(1)	–0.0010(2)	–0.0002(1)
Ga4	16*g*	1	0.24534(7)	0.08882(3)	0.95650(4)	0.0121(1)	0.0137(2)	0.0104(2)	0.0123(2)	–0.0009(2)	0.0001(2)	0.0004(1)
Ga5	8*f*	1	0	0.15956(5)	0.60329(7)	0.0124(2)	0.0139(3)	0.0074(2)	0.0159(3)	0	0	0.0006(2)
Li1	8*f*	1	0	0.039(1)	0.390(2)	0.034(5)	0.055(11)	0.023(7)	0.026(7)	0	0	0.008(6)
Na1a	8*e*	0.5	¼	0.2451(5)	¼	0.0202(9)	–	–	–	–	–	–
Na1b	16*g*	0.25	0.211(2)	0.2411(9)	0.289(1)	0.0341(12)	–	–	–	–	–	–

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor, which is exp $(-2\pi^2 [h^2a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}])$

Table S3 Ga–Ga interatomic distances in $NaLiGa_7$.The distances are classified in exo- and endo-bonds of the Ga_{12} icosahedron (Ga1–Ga4) and the 4-bonded atom (Ga5).

Ga–Ga	***d* / Å**		
Ga1–Ga5	2.588(1)	1×	exo
–Ga4	2.6419(8)	2×	endo
–Ga3	2.6868(8)	2×	endo
–Ga5	2.7710(1)	1×	endo
Ga2–Ga5	2.522(1)	1×	exo
–Ga4	2.6619(7)	2×	endo
–Ga3	2.6945(8)	2×	endo
–Ga1	2.771(1)	1×	endo
Ga3–Ga3	2.5054(7)	1×	exo
–Ga4	2.5981(8)	1×	endo
–Ga4	2.6326(7)	1×	endo
–Ga3	2.6407(8)	1×	endo
–Ga1	2.6868(8)	1×	endo
–Ga2	2.6945(8)	1×	endo
Ga4–Ga5	2.5145(7)	1×	exo
–Ga3	2.5981(8)	1×	endo
–Ga3	2.6326(7)	1×	endo
–Ga1	2.6419(8)	1×	endo
–Ga2	2.6619(7)	1×	endo
–Ga4	2.8152(7)	1×	endo
Ga5–Ga4	2.5145(7)	2×	
–Ga2	2.522(1)	1×	4b
–Ga1	2.588(1)	1×	

Table S4 Ga–Ga–Ga bond angles in the Ga_{12} icosahedron of $NaLiGa_7$.

∡Ga–Ga–Ga	Deg / °		∡Ga–Ga–Ga	Deg / °	
Ga2–**Ga1**–Ga3	105.80(1)	4×	Ga1–**Ga2**–Ga3	103.31(1)	4×
Ga2–**Ga1**–Ga4	58.86(1)	4×	Ga1–**Ga2**–Ga4	58.15(1)	4×
Ga3–**Ga1**–Ga3	58.87(1)	2×	Ga3–**Ga2**–Ga3	58.68(1)	2×
Ga3–**Ga1**–Ga4	59.21(2)	4×	Ga3–**Ga2**–Ga4	58.03(2)	4×
Ga3–**Ga1**–Ga4	105.64(2)	4×	Ga3–**Ga2**–Ga4	104.12(2)	4×
Ga4–**Ga1**–Ga4	105.33(2)	2×	Ga4–**Ga2**–Ga4	104.21(2)	2×
Ga1–**Ga3**–Ga2	113.08(2)	4×	Ga1–**Ga4**–Ga2	62.99(1)	4×
Ga1–**Ga3**–Ga3	60.57(1)	4×	Ga1–**Ga4**–Ga3	61.25(2)	4×
Ga1–**Ga3**–Ga4	59.55(2)	4×	Ga1–**Ga4**–Ga3	109.79(3)	4×
Ga1–**Ga3**–Ga4	112.97(2)	4×	Ga1–**Ga4**–Ga4	107.65(2)	4×
Ga2–**Ga3**–Ga3	60.66(2)	4×	Ga2–**Ga4**–Ga3	61.61(2)	4×
Ga2–**Ga3**–Ga4	60.36(2)	4×	Ga2–**Ga4**–Ga3	110.62(3)	4×
Ga2–**Ga3**–Ga4	113.85(2)	4×	Ga2–**Ga4**–Ga4	109.14(2)	4×
Ga3–**Ga3**–Ga4	107.24(2)	4×	Ga3–**Ga4**–Ga3	104.05(2)	4×
Ga3–**Ga3**–Ga4	107.48(3)	4×	Ga3–**Ga4**–Ga4	56.85(2)	4×
Ga4–**Ga3**–Ga4	65.12(2)	4×	Ga3–**Ga4**–Ga4	58.03(2)	4×

Table S5 Ga–Ga–Ga bond angles for the 4-bonded Ga atoms of $NaLiGa_7$.

∡Ga–Ga–Ga	Deg / °	
Ga1–**Ga5**–Ga2	123.83(4)	1×
Ga1–**Ga5**–Ga4	97.59(1)	2×
Ga2–**Ga5**–Ga4	108.99(1)	2×
Ga4–**Ga5**–Ga4	120.26(2)	1×

Table S6 DTA measurements of Na_2Ga_7, $Na_{1.8}Li_{0.2}Ga_7$ and $NaLiGa_7$. Presented are endothermal effects on heating and products after cooling identified by PXRD. Temperatures for the first effect represent the onset temperature, those for the second effect are estimated. The experimental error for the first effect is lower than 2 °C.

Composition	**1st effect *T* / °C**	**2nd effect *T* / °C**	**Final products**
Na_2Ga_7[1]	501	515	Na_7Ga_{13},[2] $NaGa_4$,[3] Ga
$Na_{1.8}Li_{0.2}Ga_7$	498	509	$Na_{2-x}Li_xGa_7$, $NaGa_4$, unknown
$NaLiGa_7$	489	505	$Na_{2-x}Li_xGa_7$ and $LiGa_2$[4]

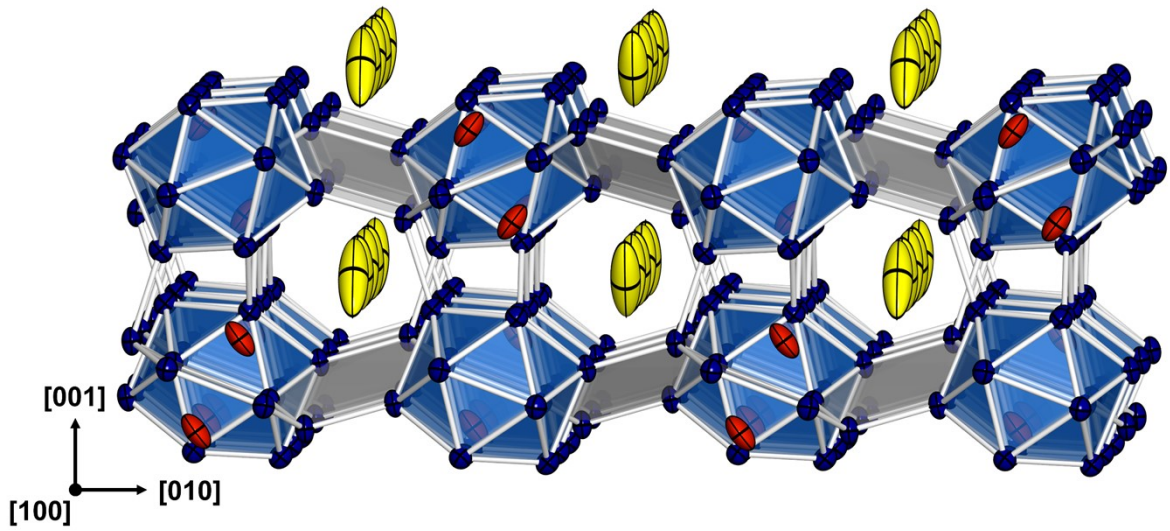


Fig. S1 Structure model of $NaLiGa_7$, view along [100]. The ADPs of Na1 (yellow, 95 % probability) show a large and cigar-shaped ellipsoid. Li1 atoms (red) occupy caves between three icosaheda.

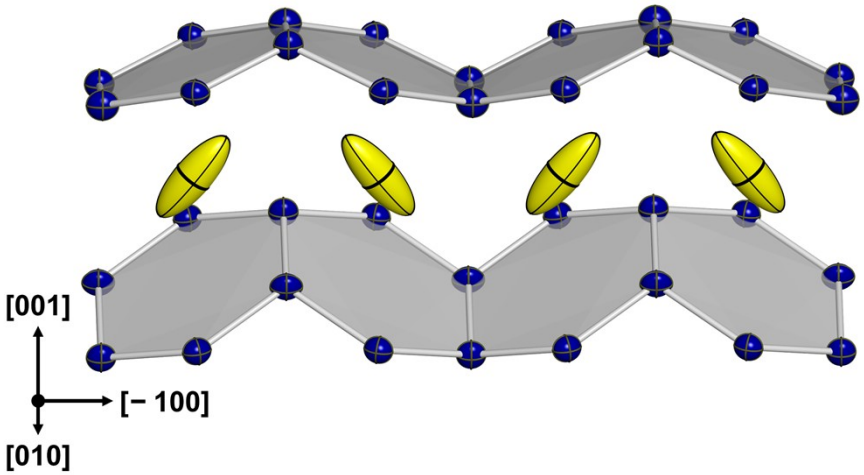


Fig. S2 Orientation of the Na1 ellipsoids (yellow, 95 % probability) aligning to the walls.

Table S7a Crystallographic data for $Na_{1.8}Li_{0.2}Ga_7$ obtained from PXRD data.

Crystal system; space group	orthorhombic, *Pnma* (no. 62)
a / Å	14.847(3)
b / Å	8.646(2)
c / Å	11.558(3)
V / Å^3	1483.7(6)
Z	8
Diffractometer	Guinier-Huber Image Plate Camera G670
λ / Å	1.54056 (Cu*K*α1)
Temperature / K	293
2θ; $\sin\theta/\lambda$ (max)	100.30; 0.498
Reflections used for refinement	839
Parameters refined	137
R_I; R_p	0.0604; 0.0352

The lattice parameters were refined from individual peak positions extracted from the powder diffraction pattern by using LaB_6 as internal standard. Standard deviations were calculated considering the Berar factor of 5.09.

Table S7b Atomic coordinates and displacement parameters (in Å^2) for $Na_{1.8}Li_{0.2}Ga_7$.

Atom	**Site**	**Occupancy**	***x / a***	***y / b***	***z / c***	U_{iso}
Ga1	4*c*	1	0.6521(2)	¼	0.8241(4)	0.0079(3)
Ga2	4*c*	1	0.8624(2)	¼	0.1835(4)	0.0099(3)
Ga3	4*c*	1	0.9253(3)	¼	0.9501(4)	0.0139(3)
Ga4	4*c*	1	0.5761(3)	¼	0.0420(4)	0.0113(3)
Ga5	8*d*	1	0.8043(2)	0.0928(3)	0.8348(3)	0.0095(3)
Ga6	8*d*	1	0.7056(2)	0.0966(3)	0.1685(3)	0.0094(3)
Ga7	8*d*	1	0.6654(2)	0.0028(5)	0.9577(2)	0.0138(3)
Ga8	8*d*	1	0.8444(2)	0.0031(5)	0.0477(2)	0.0091(3)
Ga9	4*c*	1	0.0871(3)	¼	0.8811(3)	0.0093(3)
Ga10	4*c*	1	0.4120(3)	¼	0.1032(3)	0.0122(3)
Na1	4*c*	0.48(2)	0.291(1)	¼	0.895(2)	0.01867(7)
Li1	4*c*	0.52(2)	0.291(1)	¼	0.895(2)	0.01867(7)
Na2	4*c*	0.79(1)	0.0964(9)	¼	0.133(1)	0.01867(7)
Na3	8*d*	1	0.4909(5)	0.0349(7)	0.8159(6)	0.034(2)

Table S8a Crystallographic data for $Na_{1.5}Li_{0.5}Ga_7$ obtained from PXRD data.

Crystal system; space group	orthorhombic, *Pnma* (no. 62)
a / Å	14.834(1)
b / Å	8.5956(9)
c / Å	11.488(2)
V / Å^3	1464.8(3)
Z	8
Diffractometer	Guinier-Huber Image Plate Camera G670
λ / Å	1.54056 (Cu*K*α1)
Temperature / K	293
2θ; $\sin\theta/\lambda$ (max)	100.30; 0.498
Reflections used for refinement	826
Parameters refined	147
R_I; R_p	0.0940; 0.0581

The lattice parameters were refined from individual peak positions extracted from the powder diffraction pattern by using LaB_6 as internal standard. Standard deviations were calculated considering the Berar factor of 6.65.

Table S8b Atomic coordinates and displacement parameters (in Å^2) for $Na_{1.5}Li_{0.5}Ga_7$.

Atom	Site	Occupancy	*x / a*	*y / b*	*z / c*	U_{iso}
Ga1	4*c*	1	0.6544(3)	¼	0.8219(4)	0.0099(4)
Ga2	4*c*	1	0.8594(3)	¼	0.1862(4)	0.0159(4)
Ga3	4*c*	1	0.9266(3)	¼	0.9532(4)	0.0177(4)
Ga4	4*c*	1	0.5772(3)	¼	0.0437(4)	0.0150(4)
Ga5	8*d*	1	0.8065(2)	0.0928(4)	0.8275(3)	0.0111(3)
Ga6	8*d*	1	0.7062(2)	0.0955(4)	0.1664(3)	0.0122(3)
Ga7	8*d*	1	0.6675(2)	0.9987(4)	0.9557(3)	0.0107(3)
Ga8	8*d*	1	0.8482(2)	0.0062(4)	0.0440(3)	0.0109(4)
Ga9	4*c*	1	0.0857(3)	¼	0.8846(3)	0.0077(4)
Ga10	4*c*	1	0.4152(3)	¼	0.0992(4)	0.0137(4)
Na1a	4*c*	0.69(2)	0.088(1)	¼	0.139(2)	0.01376(9)
Na1b	4*c*	0.31(2)	0.027(2)	¼	0.141(4)	0.01385(9)
Li1	4*c*	0.38(5)	0.858(9)	¼	0.64(1)	0.01382(9)
Na2	8*d*	1	0.4910(5)	0.0497(8)	0.8235(8)	0.028(2)

Table S9a Crystallographic data for $Na_{1.2}Li_{0.8}Ga_7$ obtained from PXRD data.

Crystal system; space group	orthorhombic, *Cmce* (no. 64)
a / Å	8.5692(9)
b / Å	14.836(2)
c / Å	11.466(2)
V / Å^3	1457.7(4)
Z	8
Diffractometer	Guinier-Huber Image Plate Camera G670
λ / Å	1.54056 (Cu*K*α1)
Temperature / K	293
2θ; $\sin\theta/\lambda$ (max)	100.40; 0.499
Reflections used for refinement	413
Parameters refined	63
R_I; R_p	0.0529; 0.0248

The lattice parameters were refined from individual peak positions extracted from the powder diffraction pattern by using LaB_6 as internal standard. Standard deviations were calculated considering the Berar factor of 4.03.

Table S9b Atomic coordinates and displacement parameters (in Å^2) for $Na_{1.2}Li_{0.8}Ga_7$.

Atom	**Site**	**Occupancy**	***x / a***	***y / b***	***z / c***	U_{iso}
Ga1	8*f*	1	0	0.1077(2)	0.8218(3)	0.018(1)
Ga2	8*f*	1	0	0.1782(3)	0.0440(2)	0.0089(7)
Ga3	16*g*	1	0.1560(3)	0.0491(2)	0.1669(2)	0.0139(5)
Ga4	16*g*	1	0.2471(2)	0.0890(2)	0.9573(1)	0.0111(4)
Ga5	8*f*	1	0	0.1618(3)	0.6056(2)	0.0128(6)
Li1	8*f*	0.44(4)	0	0.025(8)	0.391(7)	0.02*
Na1a	8*e*	0.44(2)	¼	0.235(2)	¼	0.0238(6)
Na1b	16*g*	0.56(2)	0.196(2)	0.232(2)	0.333(2)	0.0238(6)

* The parameter was fixed in the final refinement cycle.

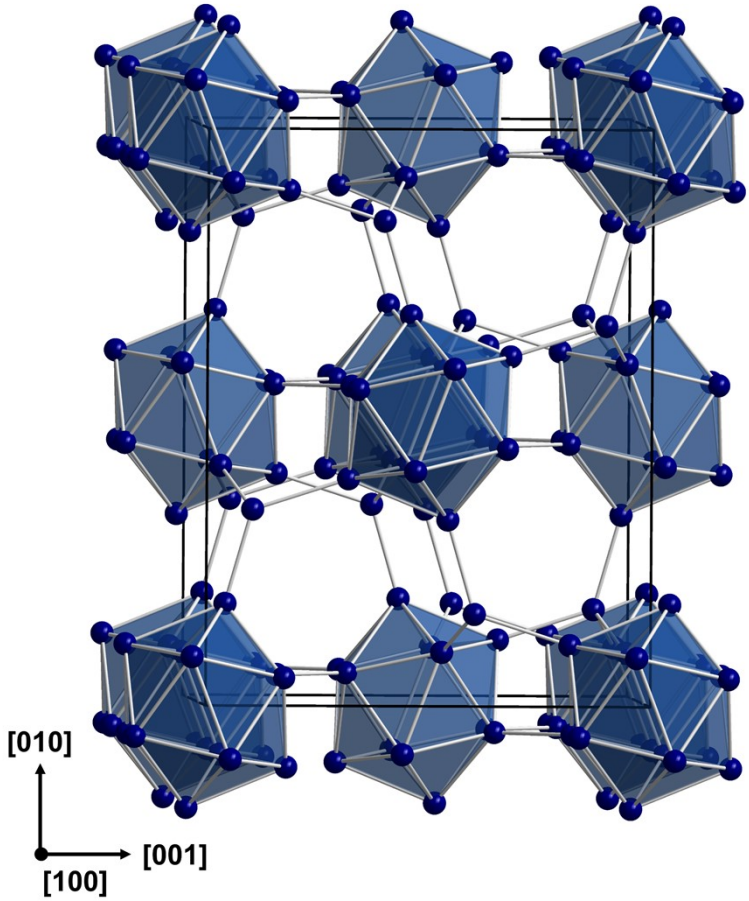


Fig. S3 In the Ga framework in $NaLiGa_7$, the centers of the Ga_{12} icosahedra exhibit an *fcc*-like arrangement.

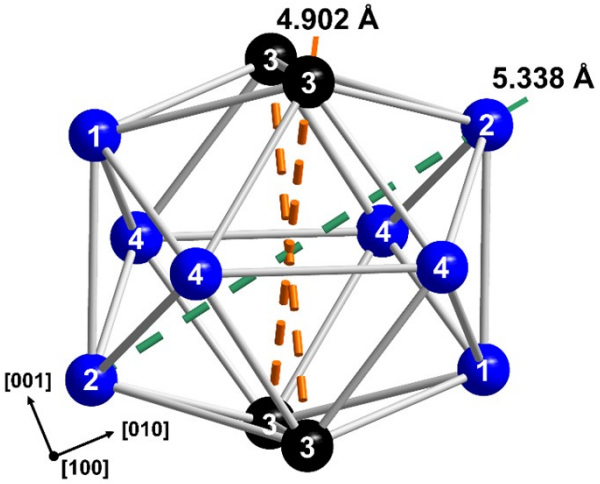


Fig. S4 Distorted Ga icosahedron in $NaLiGa_7$ with different distances of atoms in *trans*-position. Atoms connected with 4-bonded Ga atoms are drawn in blue, atoms connected to an adjacent icosahedron in black.

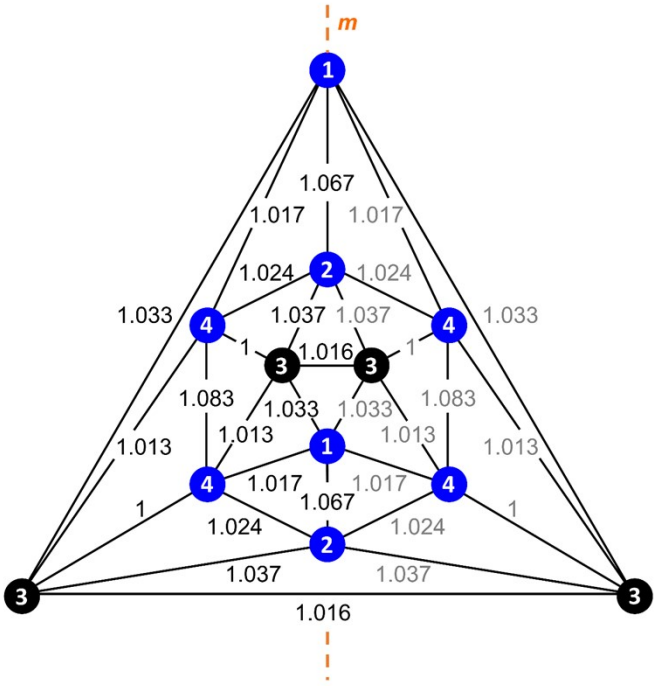


Fig. S5 Schlegel graph of the Ga_{12} icosahedron in $NaLiGa_7$ with distances normalized to the shortest Ga–Ga bond. Atoms connected with 4-bonded Ga atoms are drawn in blue, atoms forming exohedral bonds to neighboring icosahedra in black.

Table S10 Wyckoff symbols and occupancy of the cation sites **C1**, **C2** and **C3** in $NaLiGa_7$ and Na_2Ga_7.

Compound	Wyckoff and occupancy		
	C1	**C2**	**C3**
$NaLiGa_7$ ***Cmce***	8*f* (0, *y*, *z*) O	8*e* ($\frac{1}{4}$, *y*, $\frac{1}{4}$,) Na	8*f* (0, *y*, *z*) Li
Na_2Ga_7 ***Pnma***	4*c* 4*c* (*x*, $\frac{1}{4}$, *z*) Na O	8*d* (*x*, *y*, *z*) Na	4*c* 4*c* (*x*, $\frac{1}{4}$, *z*) Na O

Table S11 Results of structure refinements for samples with composition of $Na_{2-x}Li_xGa_7$ (x = 0, 0.2, 0.5, 0.8, 1). The gray shaded data originate from single-crystal diffraction, while the remaining data are from powder diffraction data. The challenge in determining partially occupied Na and Li positions allows only a qualitative interpretation of the powder data.

Compound (Z = 8)	x	**Wyckoff and occupancy**					**Sum occup. of cations**
		C1		**C2**	**C3**		
Na_2Ga_7 ***Pnma***	0	4*c* 1 Na	4*c* ○	8*d* 1 Na	4*c* 1 Na	4*c* ○	16
$Na_{1.8}Li_{0.2}Ga_7$ ***Pnma***	0.2	4*c* 0.79 Na	4*c* ○	8*d* 1 Na	4*c* 0.48 Na	4*c* 0.52 Li	15.16
$Na_{1.5}Li_{0.5}Ga_7$ ***Pnma***	0.5	4*c* 1 Na	4*c* ○	8*d* 1 Na	4*c* 0.38 Li	4*c* ○	13.52
$Na_{1.2}Li_{0.8}Ga_7$ ***Cmce***	0.8	8*f* ○		8*e* 1 Na	8*f* 0.44 Li		11.52
$NaLiGa_7$ ***Cmce***	1	8*f* ○		8*e* 1 Na	8*f* 1 Li		16

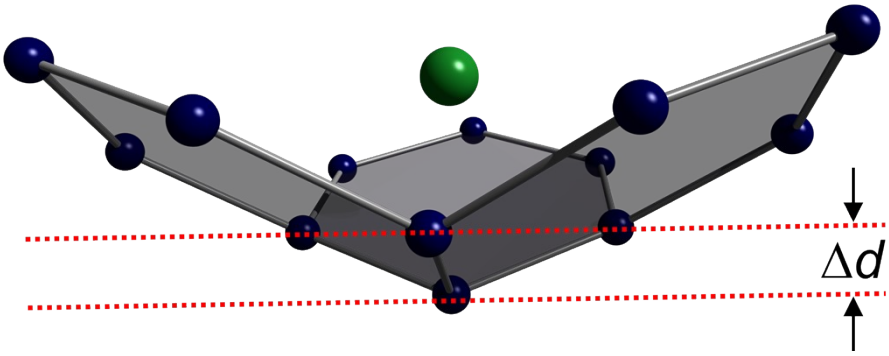
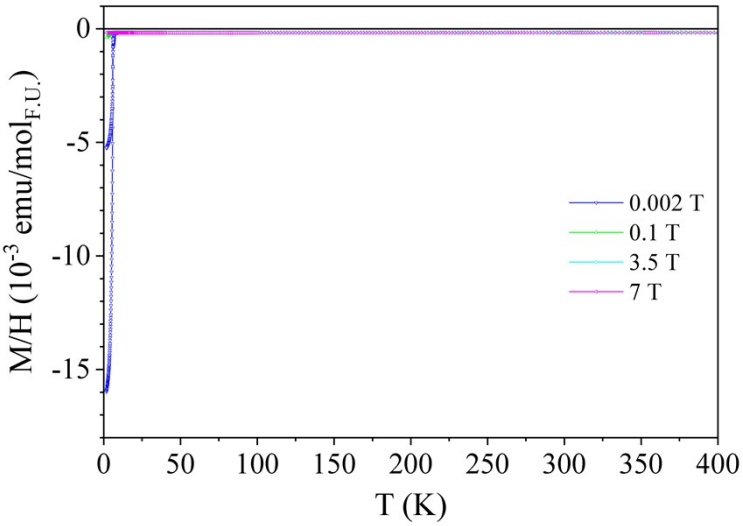


Fig. S6 Depth of **C1** hollow in the hexagonal gallium planes of the $Na_{2-x}Li_xGa_7$ crystal structure ($x < 1$) depends on the occupancy of **C1**. The distortion Δd was determined by measuring the shortest distance of the bottom Ga atom (8*d*) and the plane intersecting the three neighboring Ga atoms (8*d*, 8*d*, 4*c*) above.

(a)



(b)

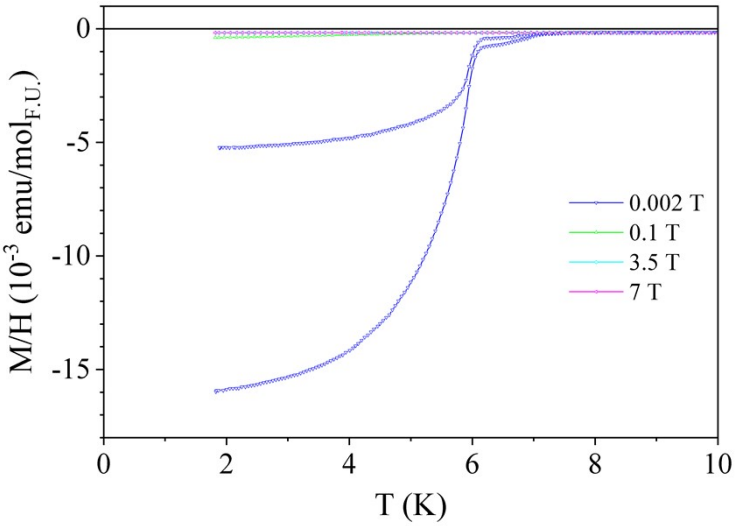


Fig. S7 (a) Temperature dependence of the magnetic susceptibility $\chi(T)$ of $NaLiGa_7$ in the temperature range T = 1.8 K - 400 K in magnetic fields $\mu_0 H$ = 0.002 T, 0.1 T, 3.5 T and 7 T. (b) Zoomed temperature range from T = 1.8 K - 10 K.

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