Supporting information for: Structural study by solid-state ^{71}Ga NMR of thin film transistor precursors

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Table of Contents

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Notes on CASTEP Calculations

Calculations were first generated using the single-crystal XRD datasets; however, the processed datasets resulted in NMR parameters that did not match the experimental results. Therefore, it was necessary to use the XRD results before the SQUEEZE transformation was applied, and it was also necessary to include 15 NO_3^- counterions surrounding the cluster to obtain reasonable approximations of the quadrupolar tensors.

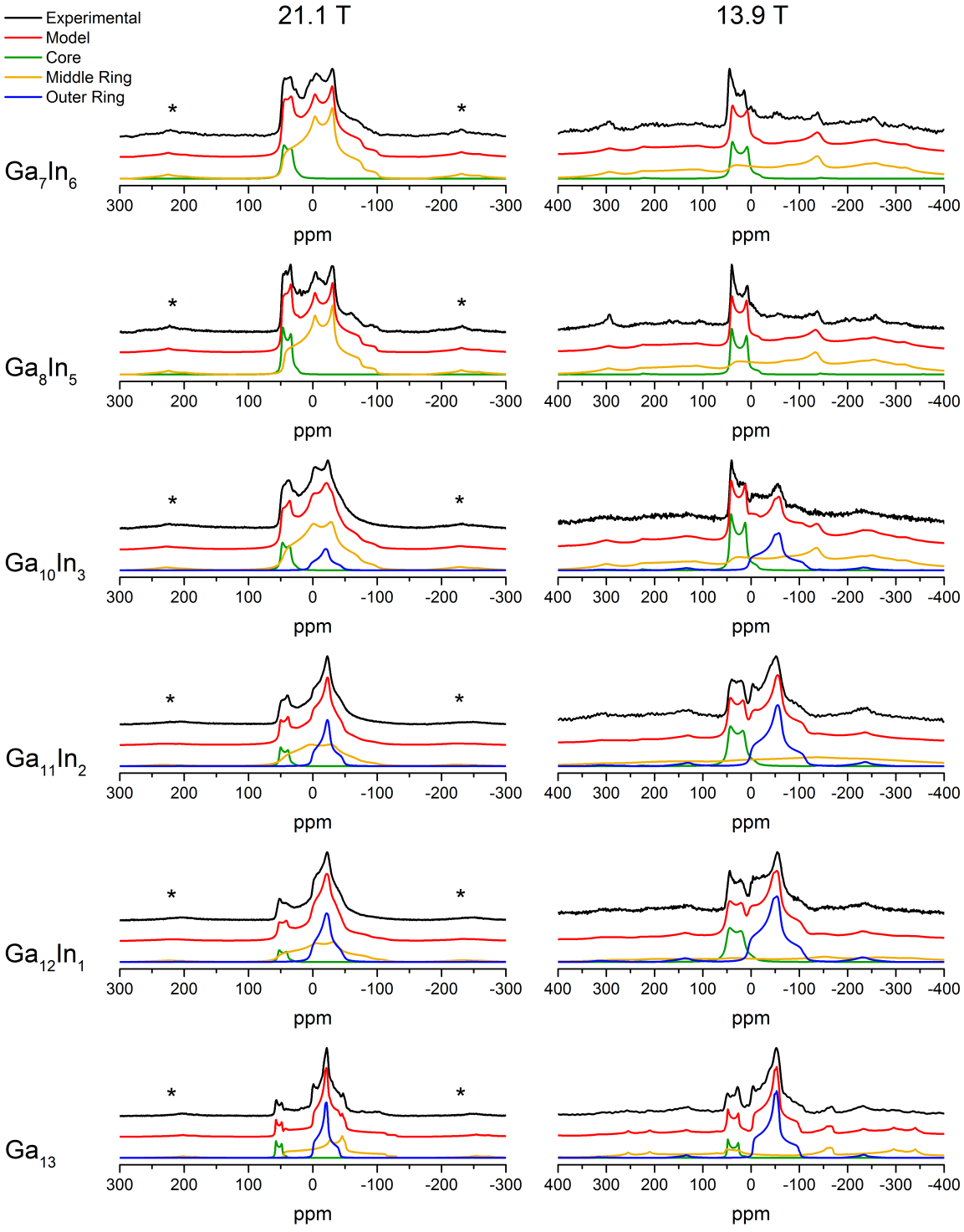

Figure S1: ^{71}Ga NMR of the $\mathbf{Ga_7In_6}$, $\mathbf{Ga_8In_5}$, $\mathbf{Ga_{11}In_2}$, $\mathbf{Ga_{12}In_1}$, and $\mathbf{Ga_{13}}$ clusters at two magnetic field strengths 21.1 T (left column) and 13.9 T (right column) and spinning at 62.5 kHz (21.1 T) and 33 kHz (13.9 T). Each plot is broken down into 3 traces: black (top) is experimental data, red (middle) is the Dmfit model composed of lineshapes in green "core," amber "middle ring," and blue "outer ring" (bottom). * denote spinning sidebands.

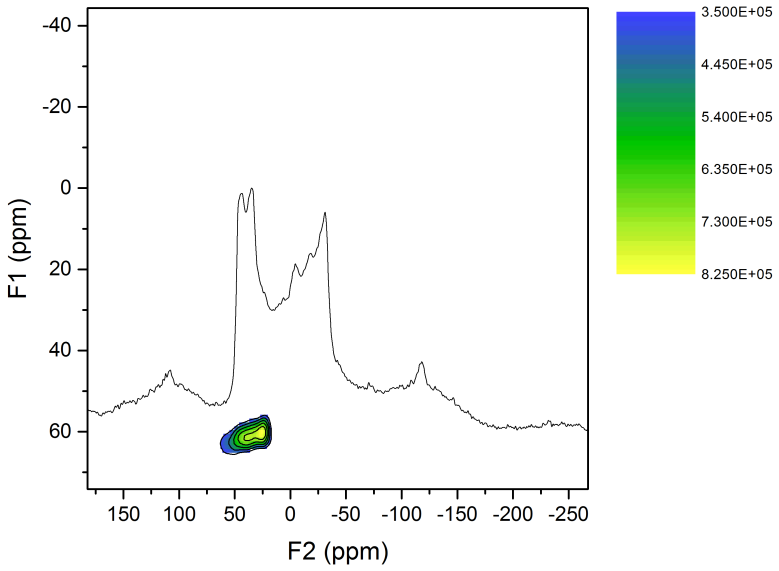

Figure S2: ^{71}Ga 3QMAS NMR experimental data at 21.1 T for the mixed heterometallic $\mathbf{Ga_7In_6}$ cluster. The core site is observed at ∼50 ppm. The gallium sites in the middle ring are not observed due to the poor efficiency of the MQMAS experiment for large C_Q sites.[S1]

Table S1: Ideal bond lengths for the heterometallic mixed metal clusters based on the volume of the polyhedra. The ideal bond length was calculated from the volume of the individual octahedra for the three metal sites.

Cluster	Volume of Octahedra (Å^3)			Ideal Bond Length (Å)		
	Core	Middle	Outer	Core	Middle	Outer
$\mathbf{Ga_7In_6}$	9.889	9.994	12.851	1.950	1.957	2.128
$\mathbf{Ga_8In_5}$	9.767	9.921	12.637	1.942	1.952	2.116
$\mathbf{Ga_{10}In_3}$	9.814	9.976	11.412	1.945	1.956	2.046
$\mathbf{Ga_{11}In_2}$	9.858	10.005	11.909	1.948	1.958	2.075
$\mathbf{Ga_{12}In_1}$	9.8567	9.9727	10.7339	1.9616	1.9557	2.0042
$\mathbf{Ga_{13}}$	9.8142	9.9717	10.1038	1.9452	1.9556	1.9642

Table S2: Dmfit simulation parameters used to model the ^{71}Ga NMR spectra at 21.1 T and 13.9 T. The simulations used "int2QUAD" to generate the NMR model.

Cluster	Fit Param.	Core	Middle Ring	Outer Ring
$\mathbf{Ga_7In_6}$	δ_{iso}, (ppm)	51.20	50.56	-
	C_Q, (MHz)	6.12	13.11	-
	η_Q	0.05	0.62	-
	EM, 21.1 T, Hz	1500	1300	-
	Amp, 21.1 T	1.97	2.02	-
	EM, 13.9 T, Hz	1500	1300	-
	Amp, 13.9 T	1.65	0.72	-
$\mathbf{Ga_8In_5}$	δ_{iso}, (ppm)	52.13	48.05	-
	C_Q, (MHz)	6.07	12.92	-
	η_Q	0.09	0.61	-
	EM, 21.1 T, Hz	990	1050	-
	Amp, 21.1 T	3.86	2.00	-
	EM, 13.9 T, Hz	700	2300	-
	Amp, 13.9 T	1.27	0.78	-
$\mathbf{Ga_{10}In_3}$	δ_{iso}, (ppm)	52.79	50.13	4.93
	C_Q, (MHz)	5.92	13.07	7.59
	η_Q	0.02	0.58	0.84
	EM, 21.1 T, Hz	1400	2600	1300
	Amp, 21.1 T	2.33	2.10	0.45
	EM, 13.9 T, Hz	1000	5000	900
	Amp, 13.9 T	2.80	0.68	0.72
$\mathbf{Ga_{11}In_2}$	δ_{iso}, (ppm)	55.29	52.74	1.54
	C_Q, (MHz)	5.87	13.39	7.31
	η_Q	0.01	0.50	0.9
	EM, 21.1 T, Hz	1100	4300	1100
	Amp, 21.1 T	1.63	1.06	1.20
	EM, 13.9 T, Hz	1200	6000	1100
	Amp, 13.9 T	3.02	0.71	1.43
$\mathbf{Ga_{12}In_1}$	δ_{iso}, (ppm)	57.58	57.59	2.56
	C_Q, (MHz)	5.84	13.97	7.47
	η_Q	0.01	0.63	0.84
	EM, 21.1 T, Hz	950	3540	1750
	Amp, 21.1 T	0.86	0.73	1.39
	EM, 13.9 T, Hz	1500	4500	1260
	Amp, 13.9 T	2.32	0.35	1.37
$\mathbf{Ga_{13}}$ [a]	δ_{iso}, (ppm)	60.7	45.6	-0.6
	C_Q, (MHz)	5.0	13.91	6.7
	η_Q	0.0	0.8	0.9
	EM, 21.1 T, Hz	542	300	630
	Amp, 21.1 T	1.78	0.38	1.32
	EM, 13.9 T, Hz	500	500	500
	Amp, 13.9 T	2.30	0.14	1.39

a) $\mathbf{Ga_{13}}$ parameters are reproduced from reference Ma et al. [S2].

References

(S1) Wu, G.; Rovnyak, D.; Griffin, R. G. *Journal of the American Chemical Society* **1996**, *118*, 9326–9332.

(S2) Ma, Z. L.; Wentz, K. M.; Hammann, B. A.; Chang, I.-Y.; Kamunde-Devonish, M. K.; Cheong, P. H.-Y.; Johnson, D. W.; Terskikh, V. V.; Hayes, S. E. *Chemistry of Materials* **2014**, *26*, 4978–4983.