

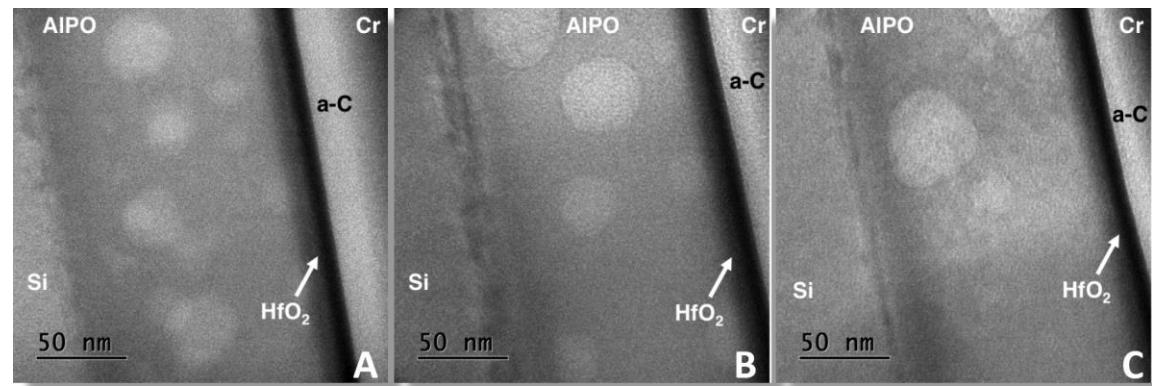
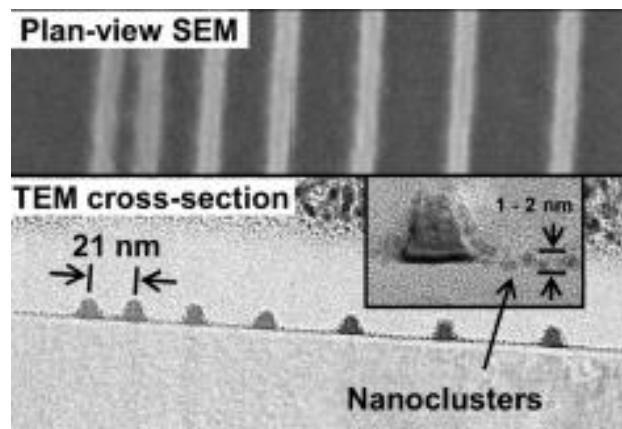
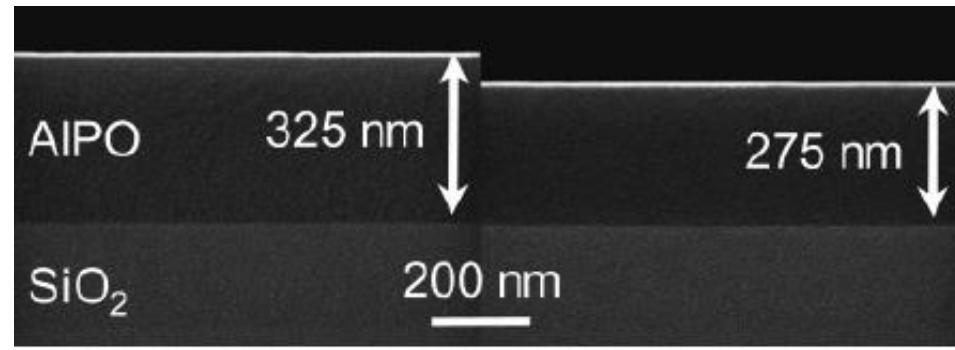
11/17/2015

CSMC

NMR of Half-Integer Quadrupolar Nuclei in Materials: Opportunities at Ultrahigh Fields

Sophia Hayes
Washington University in St. Louis

Modern Materials Science Needs New Tools for Structure Determination



Real Materials – Apple Displays

iMac
with Retina 5K display



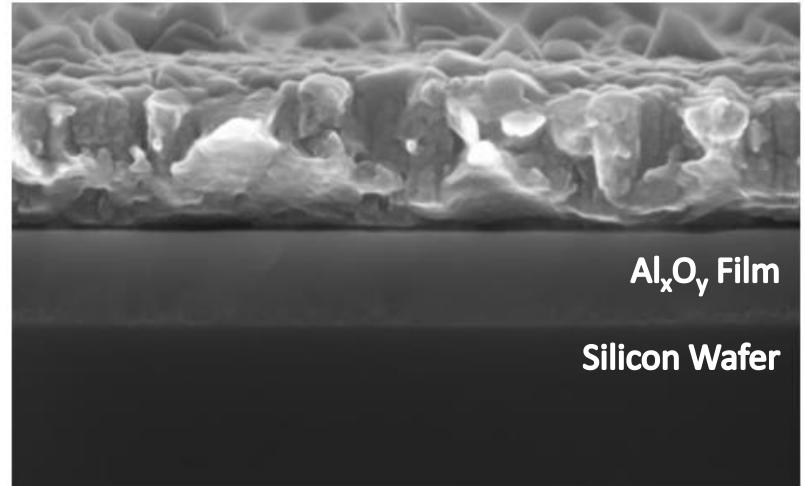
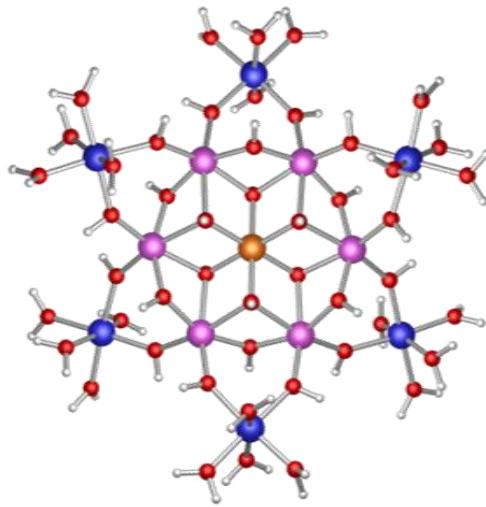
Oxide TFT

“..we took cues from the groundbreaking oxide thin film transistor ...”

Patent

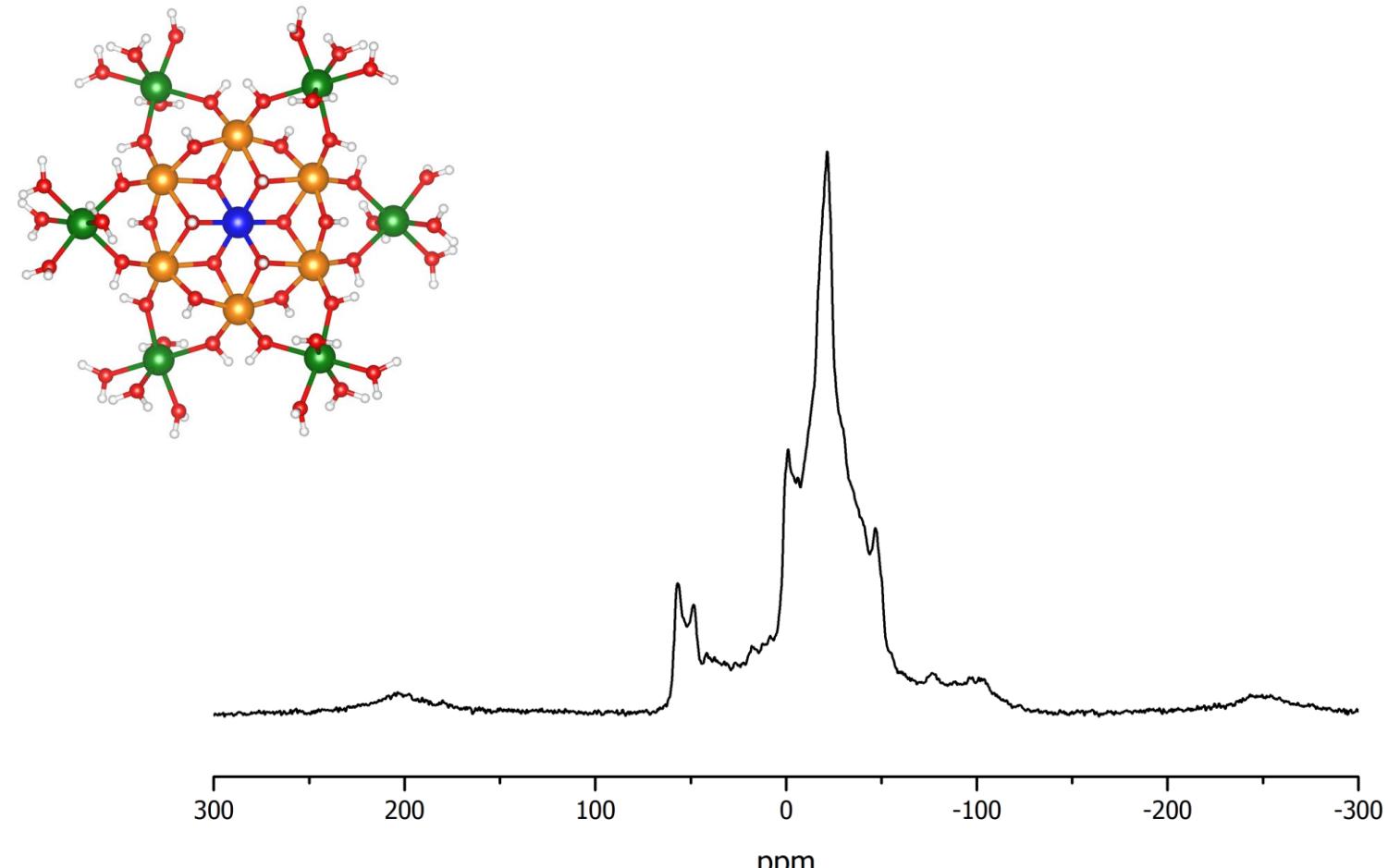
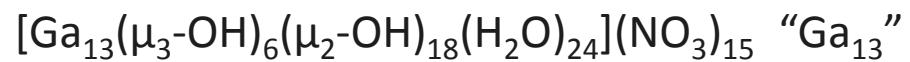
“Embodiments described herein may provide an oxide thin-film transistor (TFT) ... the semiconductor layer may include or incorporate other materials, for example, zinc oxide (**ZnO**), indium oxide (**InO**), gallium oxide (**GaO**), tin oxide (**SnO₂**), indium gallium oxide (**IGO**), indium zinc oxide (**IZO**), zinc tin oxide (**ZTO**), and indium zinc tin oxide (**IZTO**) among others.”





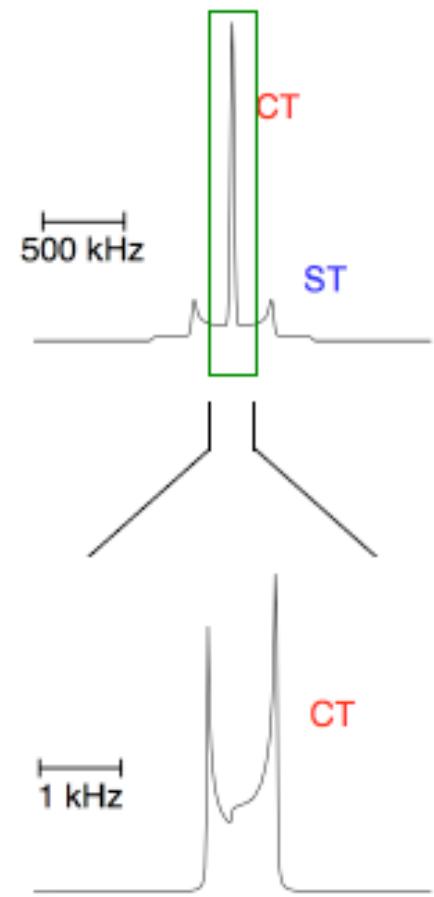
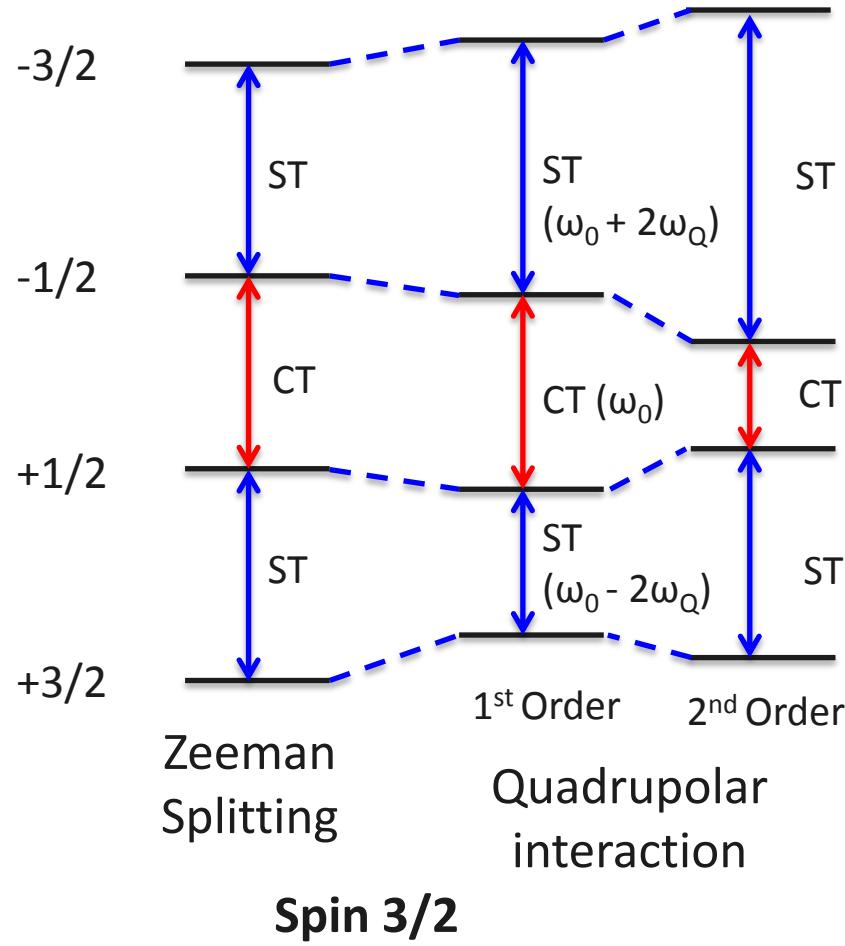
A TALE OF TWO MATERIALS: A CASE STUDY IN QUADRUPOLAR NMR (REAL MATERIALS)

Solid-state NMR



(^{71}Ga MAS, 21T Ga_{13})

Quadrupolar Nuclei



Quadrupolar Nuclei

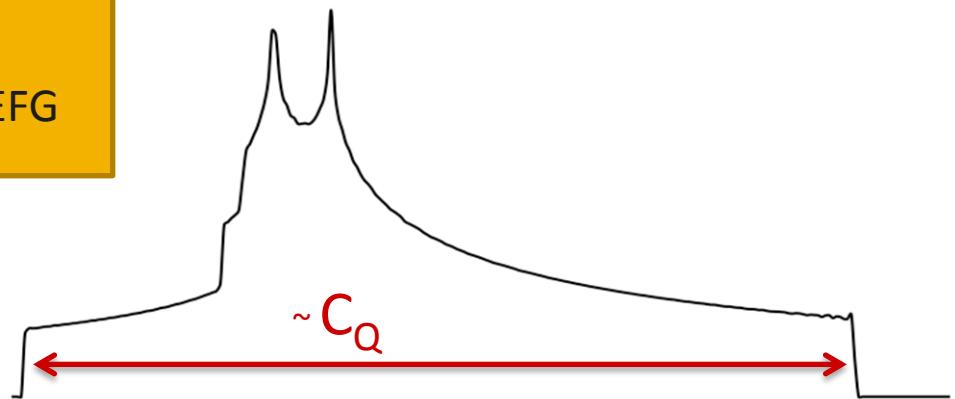
central transition lineshapes under MAS

Quadrupole Coupling Constant:

eQ = nuclear quadrupolar moment

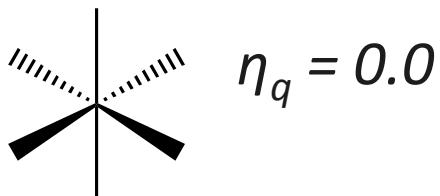
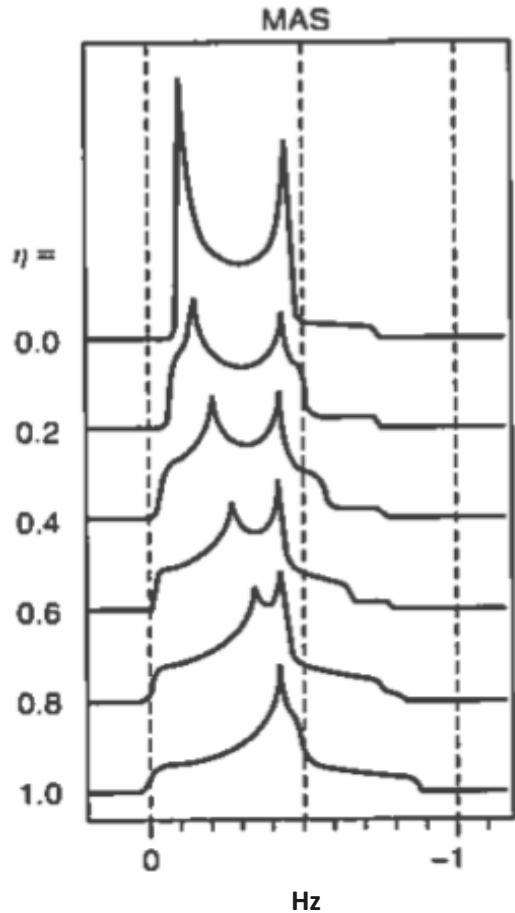
V_{zz} = largest principle component of EFG

$$C_Q = \frac{(e^2 q Q)}{h} = \frac{e Q (V_{zz})}{h}$$



Quadrupolar Nuclei

central transition lineshapes under MAS



Quadrupole Parameter:

$$\eta_q = (V_{xx} - V_{yy})/V_{zz} \quad 0 < \eta_q < 1$$

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$$

$$V_{xx} + V_{yy} + V_{zz} = 0$$



Why is field dependence important?

Second-order quadrupolar broadening

- Second-order quadrupolar frequency for an energy level/transition can be described (for $\eta_Q = 0$) by

$$\omega \propto \frac{(\omega_Q^{\text{PAS}})^2}{\omega_0} [A + B d_{00}^2(\beta) + C d_{00}^4(\beta)]$$

Constant depending upon C_Q , I and ω_0

Isotropic shift

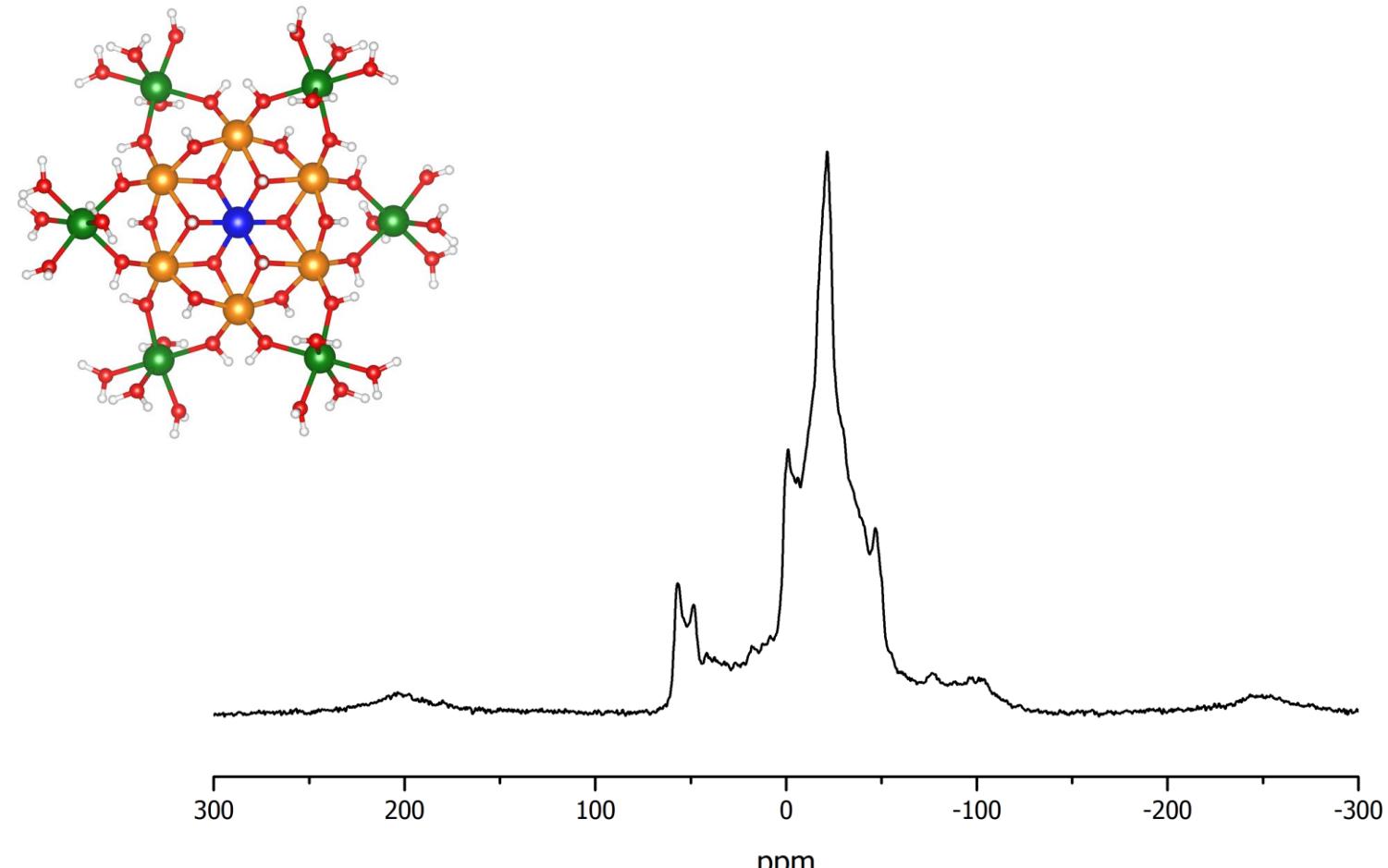
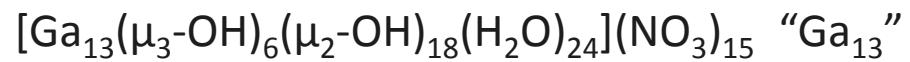
Second-rank anisotropic

Fourth-rank anisotropic

$$d_{00}^2(\theta) \propto (3 \cos^2 \theta - 1)$$

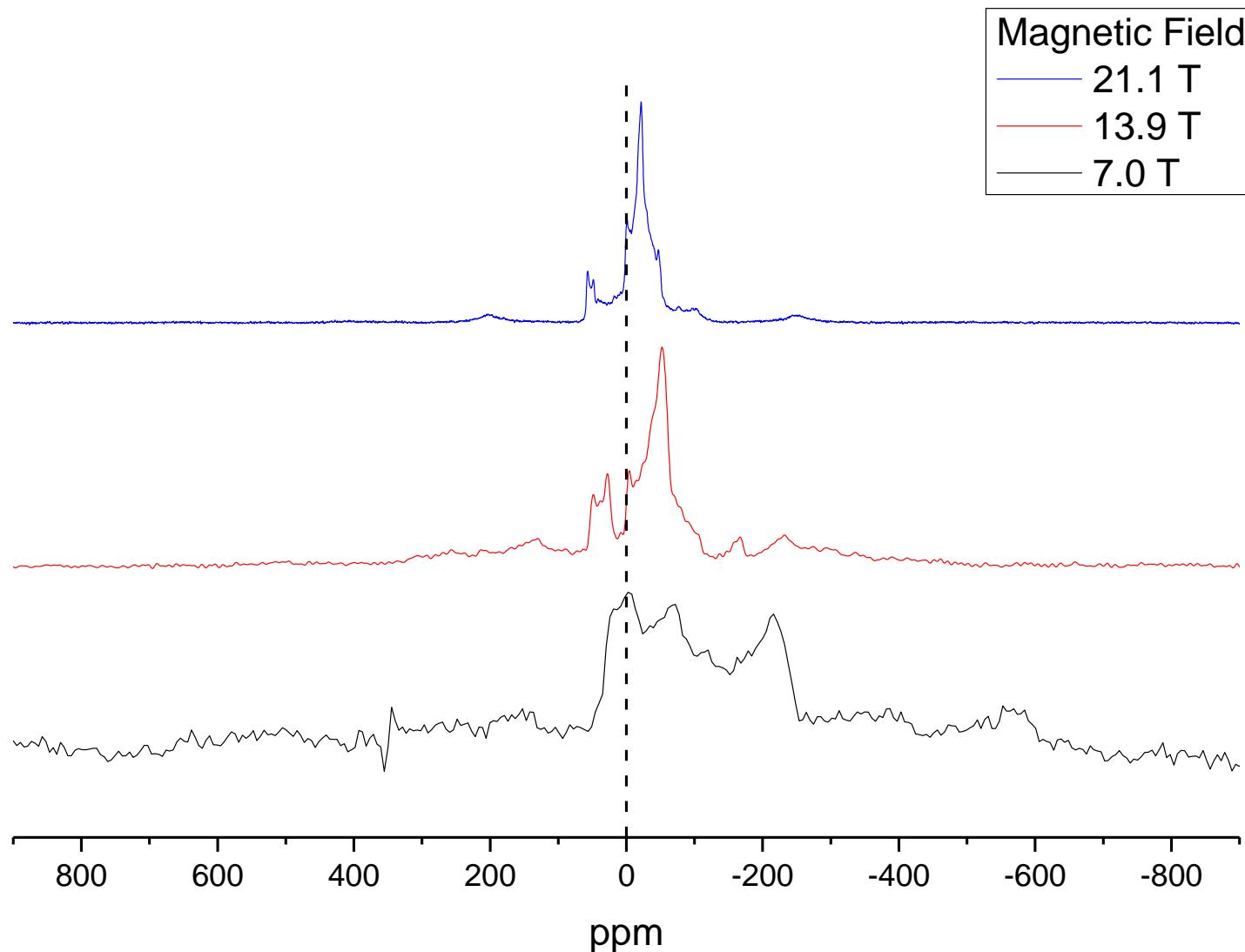
$$d_{00}^4(\theta) \propto (35 \cos^4 \theta - 30 \cos^2 \theta + 3)$$

Solid-state NMR



(^{71}Ga MAS, 21T Ga_{13})

^{71}Ga NMR - Ga_{13} Field Dependence



Multiple-Quantum Magic-Angle Spinning NMR: A New Method for the Study of Quadrupolar Nuclei in Solids

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Received August 24, 1995⁸

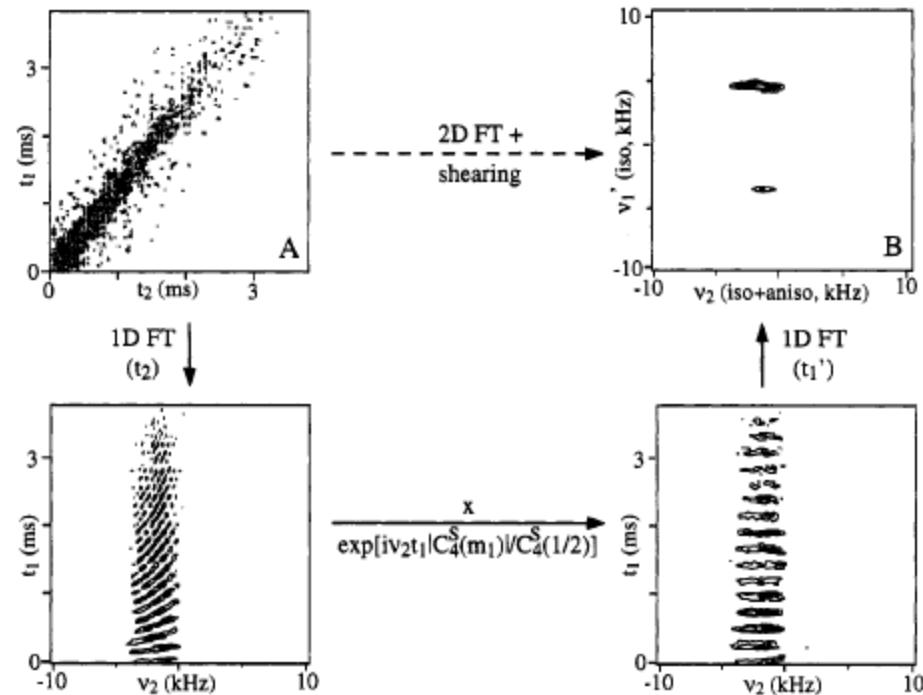


Figure 2. Two-dimensional ^{23}Na MQMAS NMR of $\text{Na}_2\text{C}_2\text{O}_4$. (A) Triple-/single-quantum correlation experiment obtained using the two-pulse sequence shown in Scheme 1. (B) Isotropic/anisotropic correlation spectrum obtained by Fourier transformation and shearing of the time-domain data; the peak at $v'_1 \approx 4$ kHz corresponds to the main resonance, the peak at $v'_1 = -3$ kHz is a spinning sideband. The shearing was implemented as illustrated in the bottom part of the figure, via a first-order t_1 -dependent phase correction along v_2 .

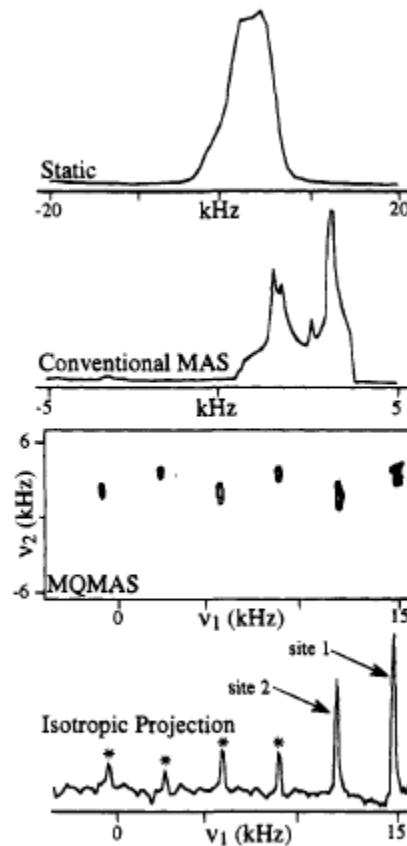
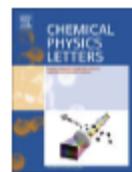


Figure 10. ^{23}Na NMR spectra of polycrystalline Na_2TeO_3 acquired under different conditions. The bottom trace corresponds to the projection of the sheared 2D MQMAS spectrum onto the isotropic (v_1) axis; asterisks correspond to spinning sidebands.



Acquisition of ultra-wideline NMR spectra from quadrupolar nuclei by frequency stepped WURST–QCPMG

Luke A. O'Dell, Aaron J. Rossini, Robert W. Schurko *

Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue, Windsor, Ontario, Canada, N9B 3P4

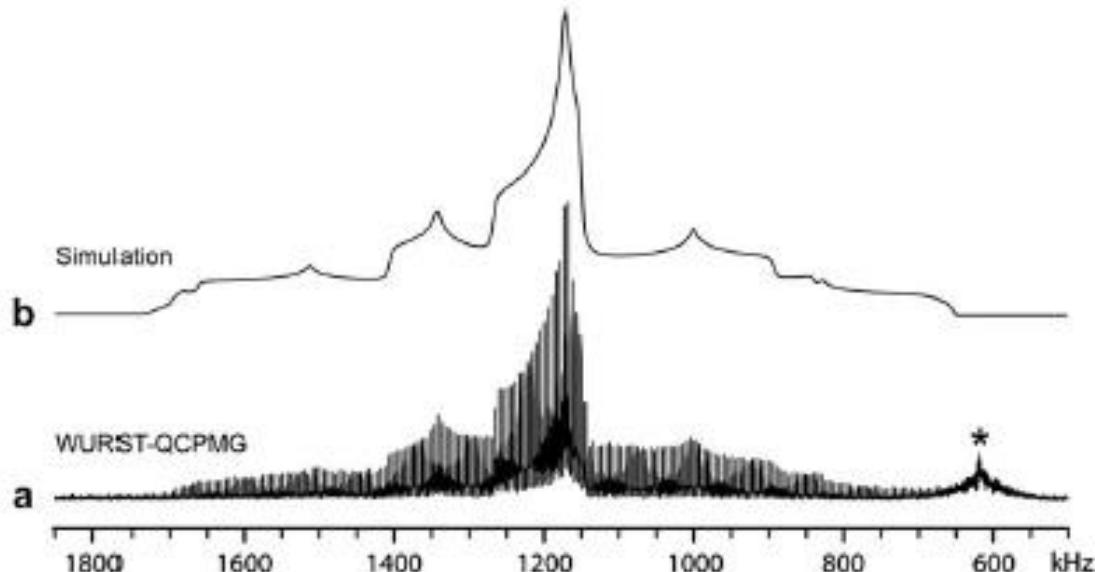


Fig. 4. (a) ^{59}Co spectrum of $\text{Co}(\text{acac})_3$ obtained using undecoupled WURST–QCPMG. The full manifold of satellite transition is excited. The asterisk denotes PM radio interference. (b) Simulation made using parameters previously reported [28].



Acquisition of ultra-wideline NMR spectra from quadrupolar nuclei by frequency stepped WURST–QCPMG

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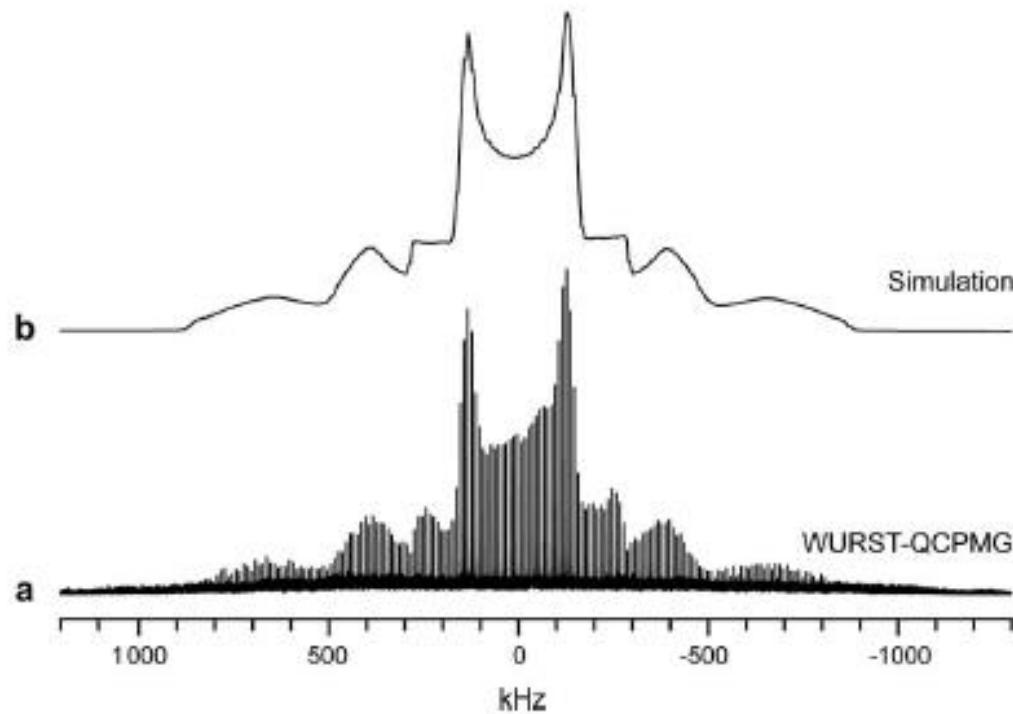
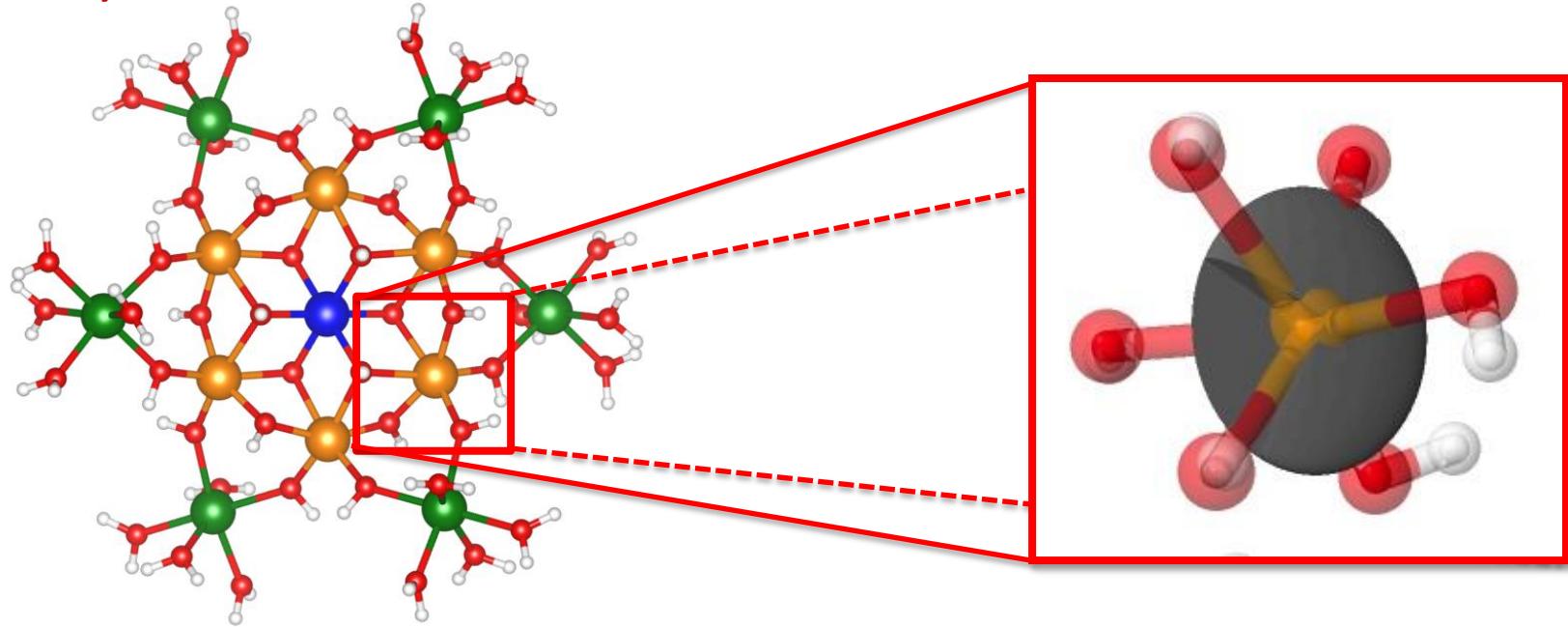


Fig. 5. (a) ^{10}B natural abundance spectrum of $v\text{-B}_2\text{O}_3$ obtained in a total experiment time of 0.8 h. (b) Simulation made using parameters previously reported [29].

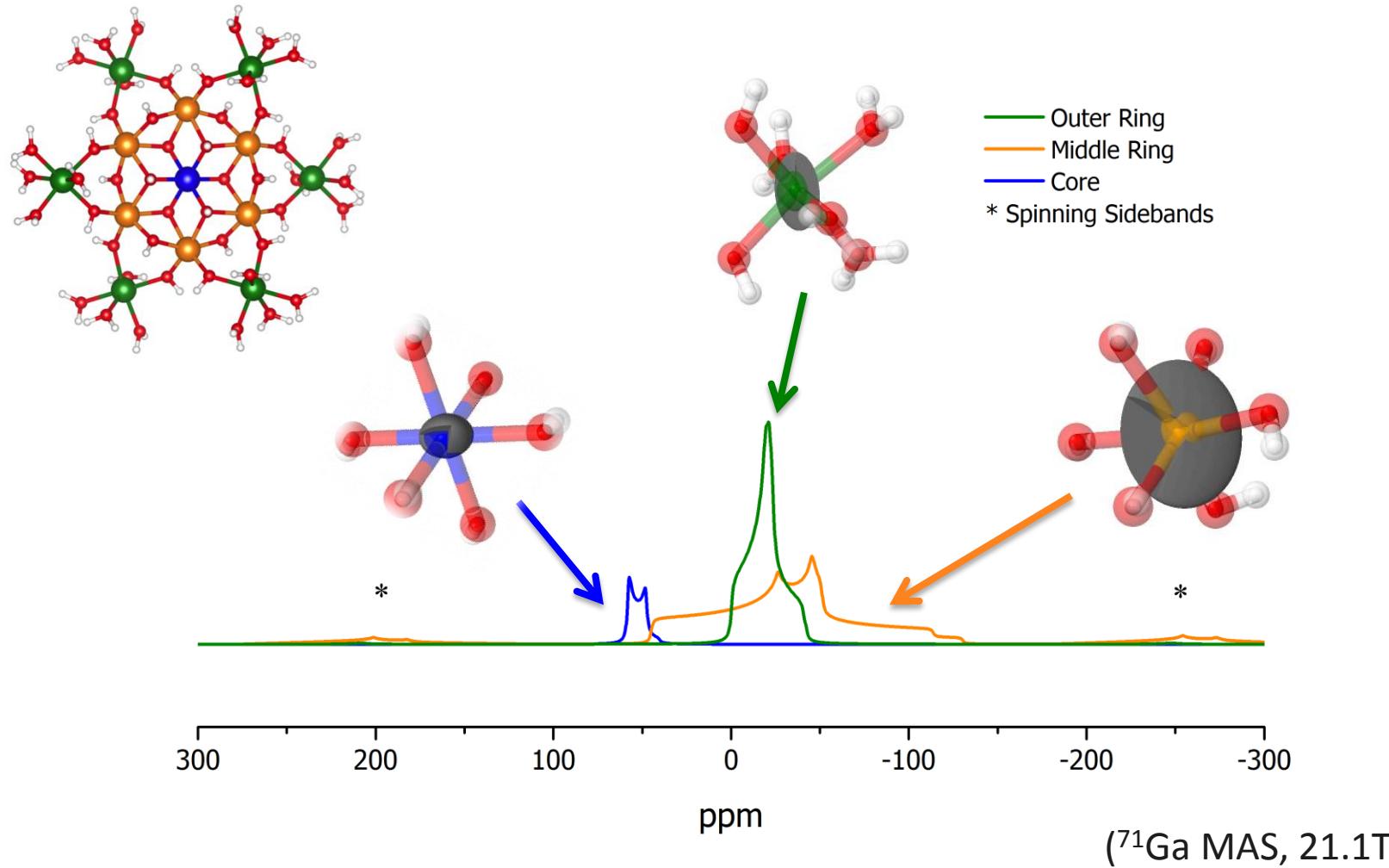
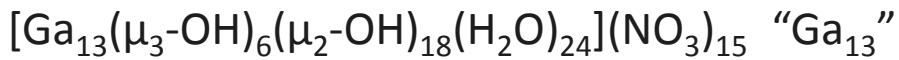
Can First Principles Calculations Help?

Electric Field Gradients (CASTEP, Quantum Espresso, VASP)

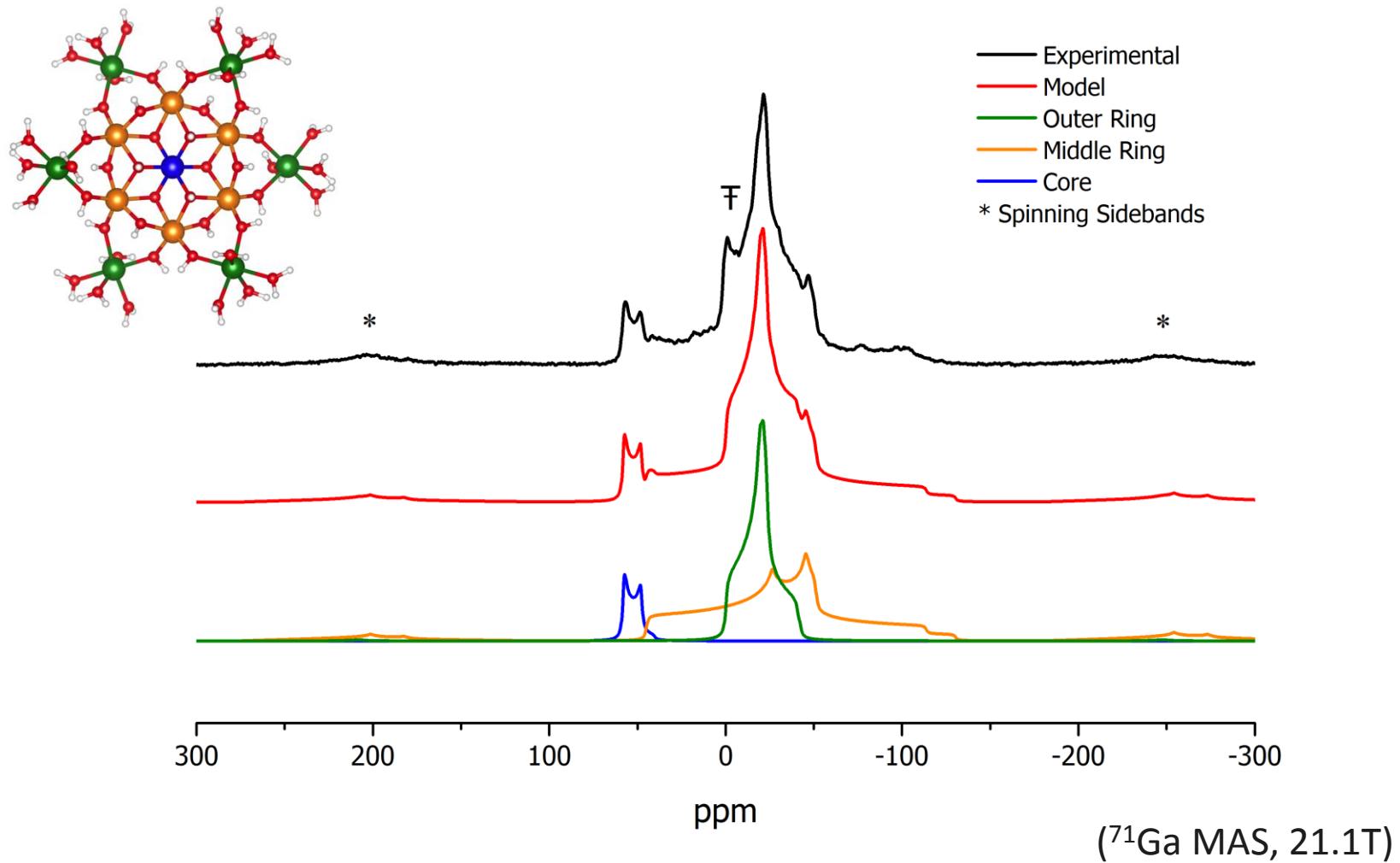
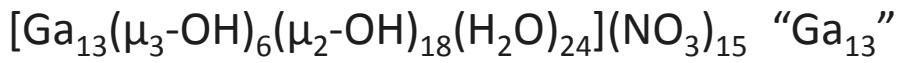


- EFG can be calculated based on a 3-D structure (the grey ellipsoid)

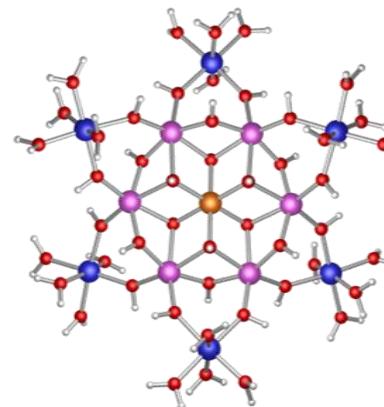
Ga_{13} NMR Model



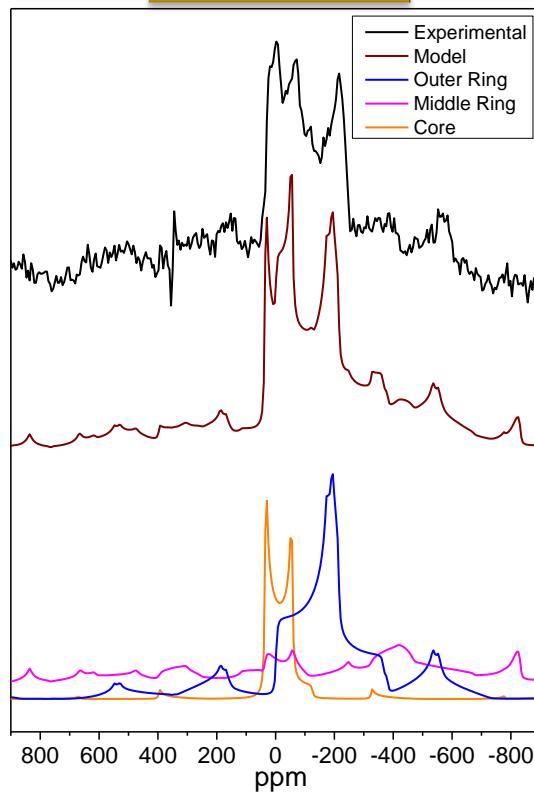
Ga₁₃ NMR Model



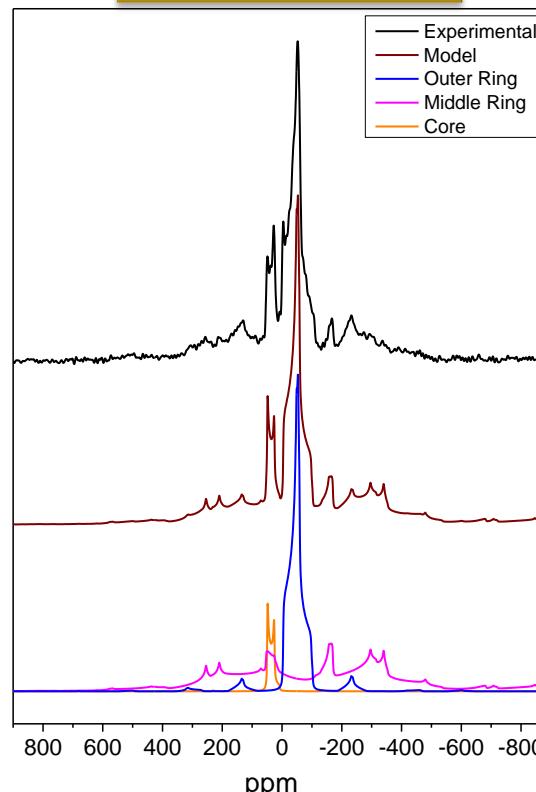
^{71}Ga NMR Ga_{13} Field Dependence



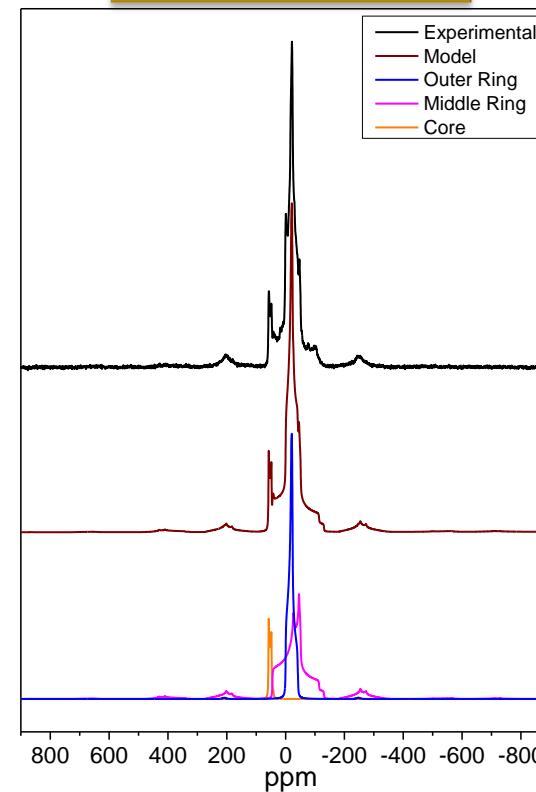
7 Tesla



13.9 Tesla



21.1 Tesla



Periodic Table of Low γ Nuclei

hydrogen 1 H 1.0079	lithium 3 Li 6.941	boron 4 Be 8.0122	carbon 6 C 12.011	nitrogen 7 N 14.0167	oxygen 8 O 15.999	fluorine 9 F 18.9985	helium 2 He 4.0026										
sodium 11 Na 22.990	magnesium 12 Mg 24.306	aluminum 13 Al 26.982	silicon 14 Si 28.095	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948										
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.982	vanadium 23 V 50.944	cromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.935	nickel 28 Ni 58.696	copper 29 Cu 63.546	zinc 30 Zn 65.402	gallium 31 Ga 69.723	germanium 32 Ge 71.033	arsenic 33 As 74.922	selenium 34 Se 78.93	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.467	strontium 38 Sr 87.620	technetium 43 Tc [99]	ruthenium 44 Ru 101.077	rhodium 45 Rh 102.905	palladium 46 Pd 106.425	silver 47 Ag 107.868	cadmium 48 Cd 112.41	cadmium 49 In 114.82	indium 50 Sn 118.71	tin 51 Sb 121.76	antimony 52 Te 127.60	tellurium 53 I 128.90	iodine 54 Xe 131.30				
cesium 55 Cs 132.91	bromine 56 Ba 136.90	lutetium 71 Lu 174.957	hafnium 72 Hf 178.490	tautium 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 190.21	osmium 76 Os 190.21	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.70	mercury 80 Hg 204.38	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 209.95	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	57-70 * lawrencium 103 Lr [262]	radutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	ununnilium 111 Uuu [272]	ununnilium 112 Uub [277]	ununquadium 114 Uuq [289]					

* Lanthanide series

** Actinide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 141.91	promethium 61 Pm [145]	europium 62 Sm [150]	gadolinium 63 Eu 151.96	ytterbium 64 Gd 152.96	terbium 65 Tb 158.95	dysprosium 66 Dy 162.93	holmium 67 Ho 164.95	erbium 68 Er 167.93	thulium 69 Tm 169.93	yterbium 70 Yb 173.99
actinium 89 Ac [227]	thorium 90 Th [230]	protactinium 91 Pa 231.04	uraniuim 92 U 235.04	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Low γ
High γ

Newly – accessible spin $\frac{1}{2}$ nuclei

Table 1. Nuclei in the region of 0 to 250 MHz at a field corresponding to 1000 MHz proton frequency

Isotope	Symbol	Name	Spin	Natural Abund.	Receptivity % (rel. to ^{13}C)	Magnetic Moment	Gamma (x 10^7 rad/Ts)	Quadrup. Moment Q/fm 2	Frequency	Reference
^{187}Os	Os	Osmium	1/2	1.96000	0.00143	0.11198	0.61929	---	22.823	OsO4
^{103}Rh	Rh	Rhodium	1/2	100.00000	0.18600	-0.15310	-0.84680	---	31.864	Rh(acac)3 p
^{57}Fe	Fe	Iron	1/2	2.11900	0.00425	0.15696	0.86806	---	32.378	Fe(CO)5
^{107}Ag	Ag	Silver	1/2	51.83900	0.20500	-0.19690	-1.08892	---	40.478	AgNO3
^{183}W	W	Tungsten	1/2	14.31000	0.06310	0.20401	1.12824	---	41.664	Na2WO4
^{109}Ag	Ag	Silver	1/2	48.16100	0.29000	-0.22636	-1.25186	---	46.535	AgNO3
^{89}Y	Y	Yttrium	1/2	100.00000	0.70000	-0.23801	-1.31628	---	49.002	Y(NO3)3
^{169}Tm	Tm	Thulium	1/2	100.00000	---	-0.40110	-2.21800	---	82.900	
^{15}N	N	Nitrogen	1/2	0.36800	0.02250	-0.49050	-2.71262	---	101.368	MeNO2
^{171}Yb	Yb	Ytterbium	1/2	14.28000	---	0.85506	4.72880	---	174.993	
^{199}Hg	Hg	Mercury	1/2	16.87000	5.89000	0.87622	4.84579	---	179.108	Me2Hgr
^{77}Se	Se	Selenium	1/2	7.63000	3.15000	0.92678	5.12539	---	190.715	Me2Se
^{29}Si	Si	Silicon	1/2	4.68320	2.16000	-0.96179	-5.31900	---	198.672	Me4Si
^{207}Pb	Pb	Lead	1/2	22.10000	11.80000	1.00906	5.58046	---	209.206	Me4Pb
^{111}Cd	Cd	Cadmium	1/2	12.80000	7.27000	-1.03037	-5.69831	---	212.155	Me2Cd
^{195}Pt	Pt	Platinum	1/2	33.83200	20.70000	1.05570	5.83850	---	214.968	Na2PtCl6
^{113}Cd	Cd	Cadmium	1/2	12.22000	7.94000	-1.07786	-5.96092	---	221.932	Me2Cd

Quadrupolar Periodic Table

IA															VIIA		
H	IIA														He		
Li	Be																
Na	Mg	IIIIB	IVB	VB	VIB	VIIIB	VIIIB		IB	IIIB							
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Rd	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Newly-Accessible Quadrupolar Nuclei @ 1 GHz

www.nyu.edu/cgi-bin/cgiwrap/aj39/NMRmap.cgi

Isotope	Symbol	Name	Spin	Natural Abund. %	Receptivity (rel. to ¹³ C)	Magnetic Moment	Gamma (x10 ⁻⁷ rad/Ts)	Quadr. Moment (Q/fm ²)	Frequency (MHz)
191	Ir	Iridium	3/2	37.3	0.06412	0.1946	0.4812	81.6	17.18
197	Au	Gold	3/2	100	0.16294	0.19127	0.47306	54.7	17.29
235	U	Uranium	7/2	0.72	---	-0.43	-0.52	493.6	18.414
193	Ir	Iridium	3/2	62.7	0.13765	0.2113	0.5227	75.1	18.71
179	Hf	Hafnium	9/2	13.62	0.43824	-0.7085	-0.6821	379.3	25.17
41	K	Potassium	3/2	6.7302	0.03341	0.2774	0.68607	7.11	25.613
167	Er	Erbium	7/2	22.93	---	-0.63935	-0.77157	356.5	28.8
155	Gd	Gadolinium	3/2	14.8	---	-0.33208	-0.82132	127	30.7
145	Nd	Neodymium	7/2	8.3	---	-0.744	-0.898	-33	33.6
161	Dy	Dysprosium	5/2	18.91	---	-0.5683	-0.9201	250.7	34.4
149	Sm	Samarium	7/2	13.82	---	-0.7616	-0.9192	7.4	34.4
73	Ge	Germanium	9/2	7.73	0.64118	-0.97229	-0.93603	-19.6	34.883
83	Kr	Krypton	9/2	11.49	1.28235	-1.07311	-1.0331	25.9	38.476
177	Hf	Hafnium	7/2	18.6	1.53529	0.8997	1.086	336.5	40.07
157	Gd	Gadolinium	3/2	15.65	---	-0.4354	-1.0769	135	40.3
147	Sm	Samarium	7/2	14.99	---	-0.9239	-1.115	-25.9	41.7
87	Sr	Strontium	9/2	7	1.11765	-1.20902	-1.16394	33.5	43.338
105	Pd	Palladium	5/2	22.33	1.48824	-0.76	-1.23	66	45.761
99	Ru	Ruthenium	5/2	12.76	0.84706	-0.7588	-1.229	7.9	46.052
39	K	Potassium	3/2	93.2581	2.8	0.50543	1.25006	5.85	46.664
163	Dy	Dysprosium	5/2	24.9	---	0.7958	1.289	264.8	48.2
173	Yb	Ytterbium	5/2	16.13	---	-0.80446	-1.3025	280	48.21
101	Ru	Ruthenium	5/2	17.06	1.59412	-0.8505	-1.377	45.7	51.614
143	Nd	Neodymium	7/2	12.2	---	-1.208	-1.457	-63	54.5
47	Ti	Titanium	5/2	7.44	0.91765	-0.93294	-1.5105	30.2	56.375
49	Ti	Titanium	7/2	5.41	1.20588	-1.25201	-1.51095	24.7	56.39
53	Cr	Chromium	3/2	9.501	0.50765	-0.61263	-1.5152	-15	56.525
40	K	Potassium	4	0.0117	0.0036	-1.45132	-1.55429	-7.3	58.02
25	Mg	Magnesium	5/2	10	1.57647	-1.0122	-1.63887	19.94	61.216
67	Zn	Zinc	5/2	4.1	0.69412	1.03556	1.67669	15	62.568
95	Mo	Molybdenum	5/2	15.92	3.06471	-1.082	-1.751	-2.2	65.169
201	Hg	Mercury	3/2	13.18	1.15882	-0.72325	-1.78877	38.6	66.116
97	Mo	Molybdenum	5/2	9.55	1.95882	-1.105	-1.788	25.5	66.537
43	Ca	Calcium	7/2	0.135	0.05106	-1.49407	-1.80307	-4.08	67.3
14	N	Nitrogen	1	99.632	5.88235	0.571	1.93378	2.044	72.263
33	S	Sulfur	3/2	0.76	0.10118	0.83117	2.05568	-6.78	76.76
189	Os	Osmium	3/2	16.15	2.32353	0.85197	2.10713	85.6	77.654
21	Ne	Neon	3/2	0.27	0.03912	-0.85438	-2.11308	10.155	78.943
176	Lu	Lutetium	7	2.59	---	3.388	2.1684	497	81.31
37	Cl	Chlorine	3/2	24.22	3.87647	0.8832	2.18437	-6.435	81.557
131	Xe	Xenon	3/2	21.18	3.50588	0.89319	2.20908	-11.4	82.439
61	Ni	Nickel	3/2	1.1399	0.24059	-0.96827	-2.3948	16.2	89.361
91	Zr	Zirconium	5/2	11.22	6.29412	-1.54246	-2.49743	-17.6	92.963
85	Rb	Rubidium	5/2	72.17	45.11765	1.60131	2.59271	27.6	96.549

Low- γ Quadrupolar Periodic Table (Living Systems)

Spin = $\frac{1}{2}$

Spin > $\frac{1}{2}$

VIIIB

IA															VIIIA		
H	IIA																
Li	Be																
Na	Mg	IIIIB	IVB	VB	VIB	VIIIB		IB	IIIB								
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Rd	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Low- γ Quadrupolar Periodic Table (Materials)

Spin = $\frac{1}{2}$

Spin > $\frac{1}{2}$

VIIIB

IA	IIA								VIIIA
H	Be								He
Li	Mg	IIIIB	IVB	VB	VIB	VIIIB	IB	IIIB	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt
Fr	Rd	Ac							
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
								Fm	Md
								No	Lr

Low- γ Quadrupolar Periodic Table

Let's imagine ... what could be next?

What can we study tomorrow that we can't do today?

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Rd	Ac		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			