NH3 FUEL ASSOCIATION

Investigating and Understanding Ionic Ammine Materials

Tuesday, 23rd September 2014

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ISIS

Science & Technology Facilities Council

A (very) brief history of ammine materials

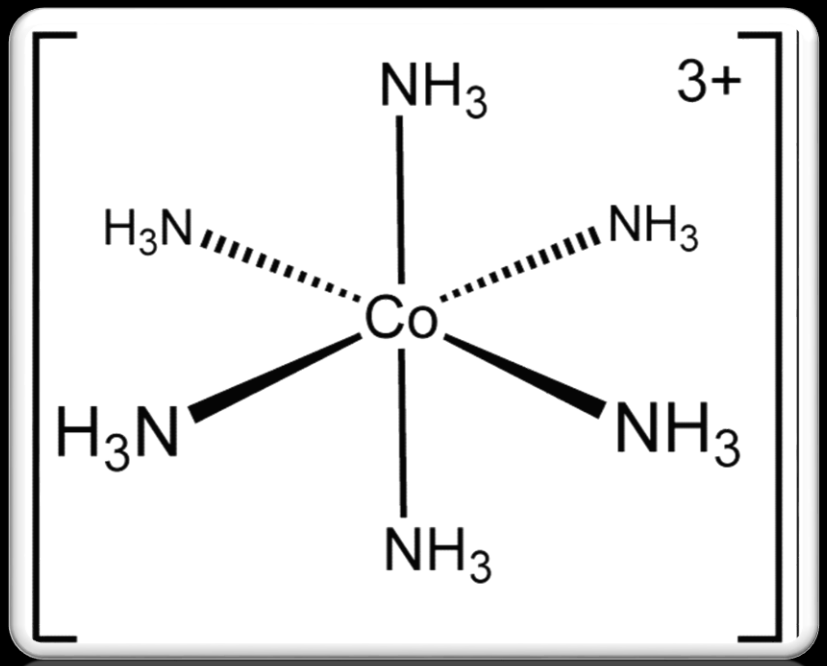
Werner Complexes

Alfred Werner
1866 – 1919
Nobel Prize in Chemistry 1913

Coordination Compounds

$CoCl_3 \bullet 6NH_3$

$[Co(NH_3)_6]Cl_3$



Conductivity and Cl^- analysis

Most Metals in Solution

Metal Ion	Ligand	Complex
Ag^{+}	2 NH_3	$Ag(NH_3)^{2+}$
Cu^{+}	2 NH_3	$Cu(NH_3)_2^{+}$
Cu^{2+}	4 NH_3	$Cu(NH_3)_4^{2+}$
Zn^{2+}	4 CN^{-}	$Zn(CN)_4^{2-}$
Hg^{2+}	4 I^{-}	HgI_4^{2-}
Co^{2+}	4 SCN^{-}	$Co(SCN)_4^{2-}$
Fe^{2+}	6 H_2O	$Fe(H_2O)_6^{2+}$
Fe^{3+}	6 H_2O	$Fe(H_2O)6^{3+}$
Fe^{2+}	6 CN^{-}	$Fe(CN)_6^{4-}$
Co^{3+}	6 NH_3	$Co(NH_3)_6^{3+}$
Ni^{2+}	6 NH_3	$Ni(NH_3)_6^{2+}$

LFSE, Cation radius and charge, nature of ligand....

THE LITHIUM BOROHYDRIDE–AMMONIA SYSTEM: PRESSURE–COMPOSITION–TEMPERATURE RELATIONSHIPS AND DENSITIES

By Edward A. Sullivan and Sidney Johnson

Contribution from the Research and Development Laboratories, Metal Hydrides, Inc., Beverly, Mass.

Received August 14, 1958

E. A. Sullivan, S. Johnson, *J. Phys. Chem*. 1959, **63**, 233 –238

$Li(NH_3)_nBH_4$

$$LiBH_4 \cdot NH_3(s) \rightleftharpoons LiBH_4(s) + NH_3(g) \quad (v)$$

$$LiBH_4 \cdot 2NH_3(s) \rightleftharpoons LiBH_4 \cdot NH_3(s) + NH_3(g) \quad (w)$$

$$LiBH_4 \cdot 3NH_3(s) \rightleftharpoons LiBH_4 \cdot 2NH_3(s) + NH_3(g) \quad (x)$$

$$LiBH_4 \cdot 4NH_3(s, \text{satd. with } LiBH_4 \cdot 3NH_3) \rightleftharpoons LiBH_4 \cdot 3NH_3(s) + NH_3(g) \quad (y)$$

$$NH_3(s) + LiBH_4 \cdot 4NH_3(s) \rightleftharpoons LiBH_4 \cdot 4NH_3(s) + NH_3(g) \quad (z)$$

E. A. Sullivan, S. Johnson, *J. Phys. Chem*. 1959, **63**, 233 –238

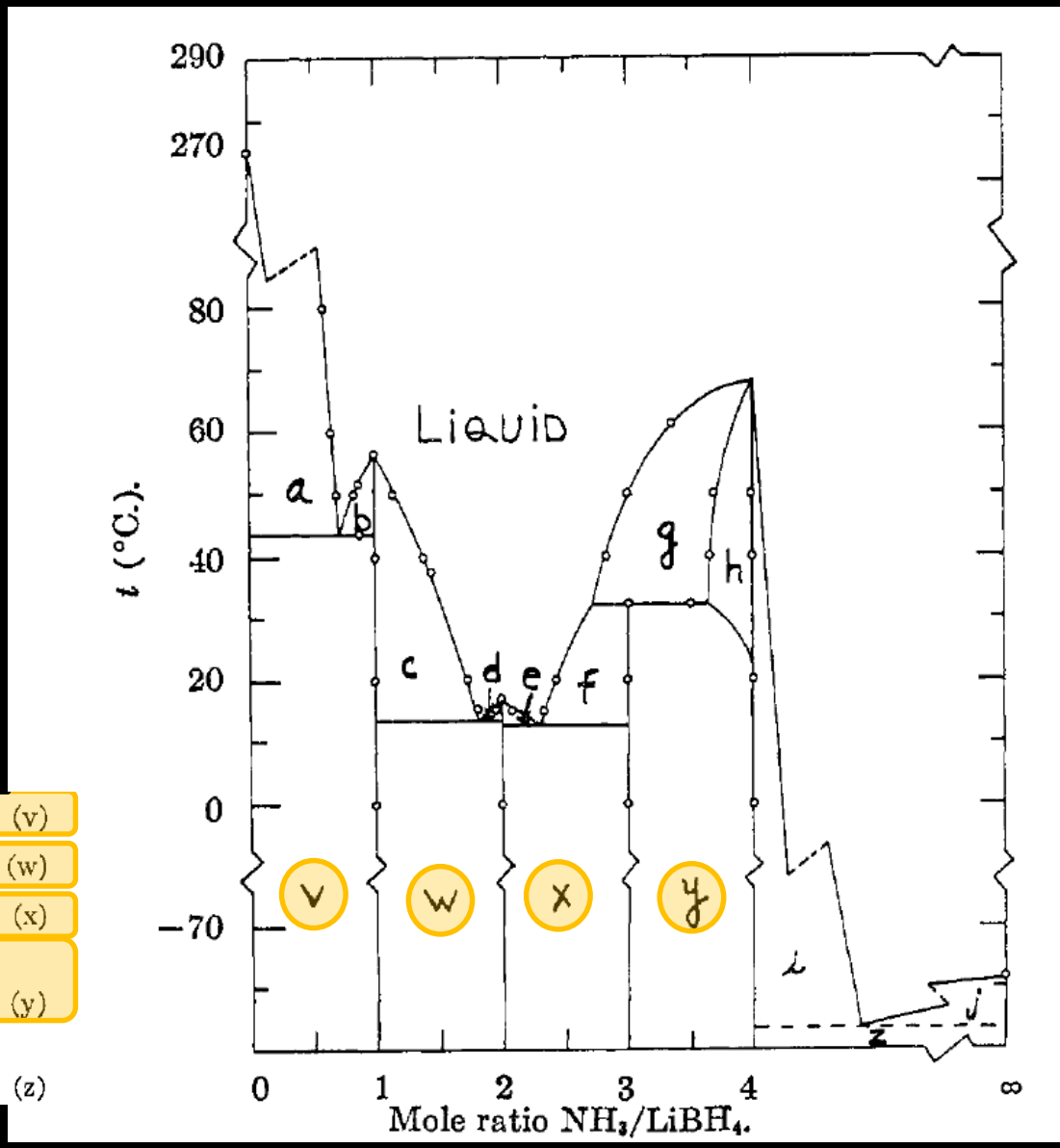
$$LiBH_4{\cdot}NH_3(s) \rightleftharpoons LiBH_4(s) + NH_3(g) \quad (v)$$

$$LiBH_4{\cdot}2NH_3(s) \rightleftharpoons LiBH_4{\cdot}NH_3(s) + NH_3(g) \quad (w)$$

$$LiBH_4{\cdot}3NH_3(s) \rightleftharpoons LiBH_4{\cdot}2NH_3(s) + NH_3(g) \quad (x)$$

$$LiBH_4{\cdot}4NH_3(s, \text{satd. with } LiBH_4{\cdot}3NH_3) \rightleftharpoons LiBH_4{\cdot}3NH_3(s) + NH_3(g) \quad (y)$$

$$NH_3(s) + LiBH_4{\cdot}4NH_3(s) \rightleftharpoons LiBH_4{\cdot}4NH_3(s) + NH_3(g) \quad (z)$$



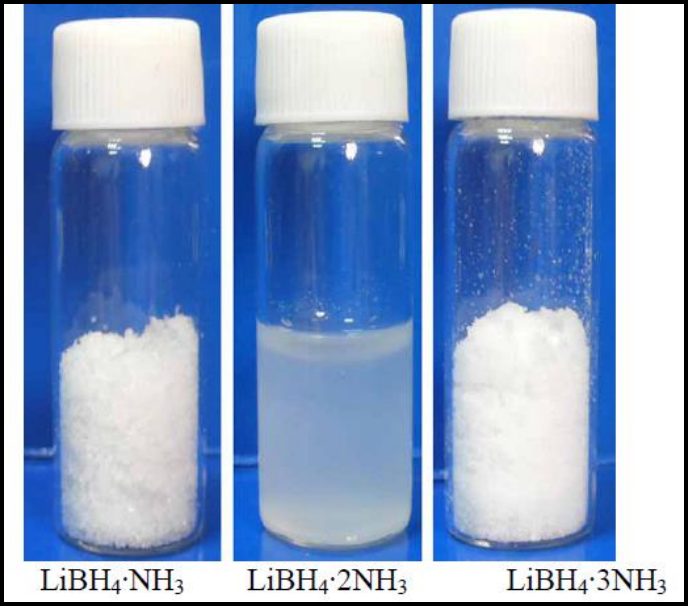
E. A. Sullivan, S. Johnson, *J. Phys. Chem*. 1959, **63**, 233 –238

$Li[NH_3]_nBH_4$

Phase n =	Ammonia Content wt%	Volume Å³	Volume of NH_3 Molecule Å³	Ammonia Density gL^{-1}	Vapour Pressure at 20°C mbar
1	41	382	43	296	6.7
2	61	588	47	385	24
3	70	652	37	526	96
4	76	840	39	539	110
Liquid NH_3 (-33°C)	100	-	-	682	1 017

C. S. Cragoe, C. H. Meyers, C. S. Taylor, *J. Am. Chem. Soc.*, 1920, **42** (2), 206–229
E. A. Sullivan and S. Johnson, *J. Phys. Chem.*, 1959, **63**, 233

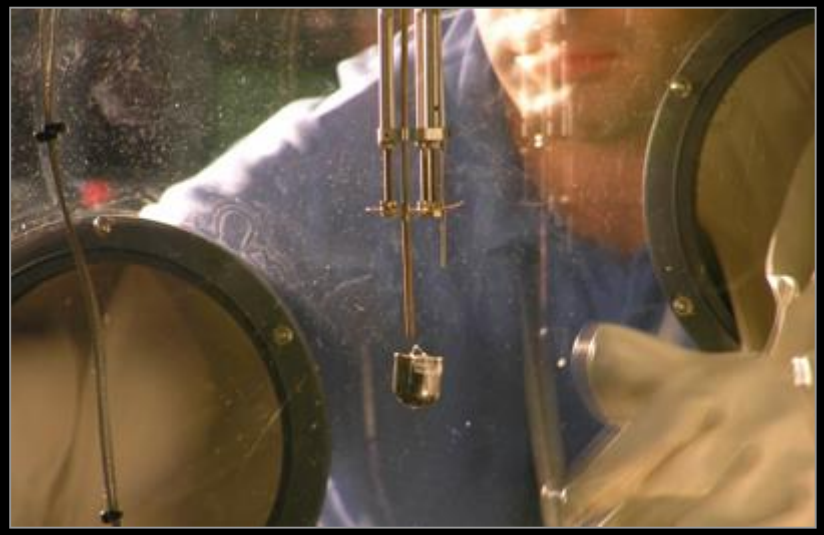
Stable just below room temperature under vacuum



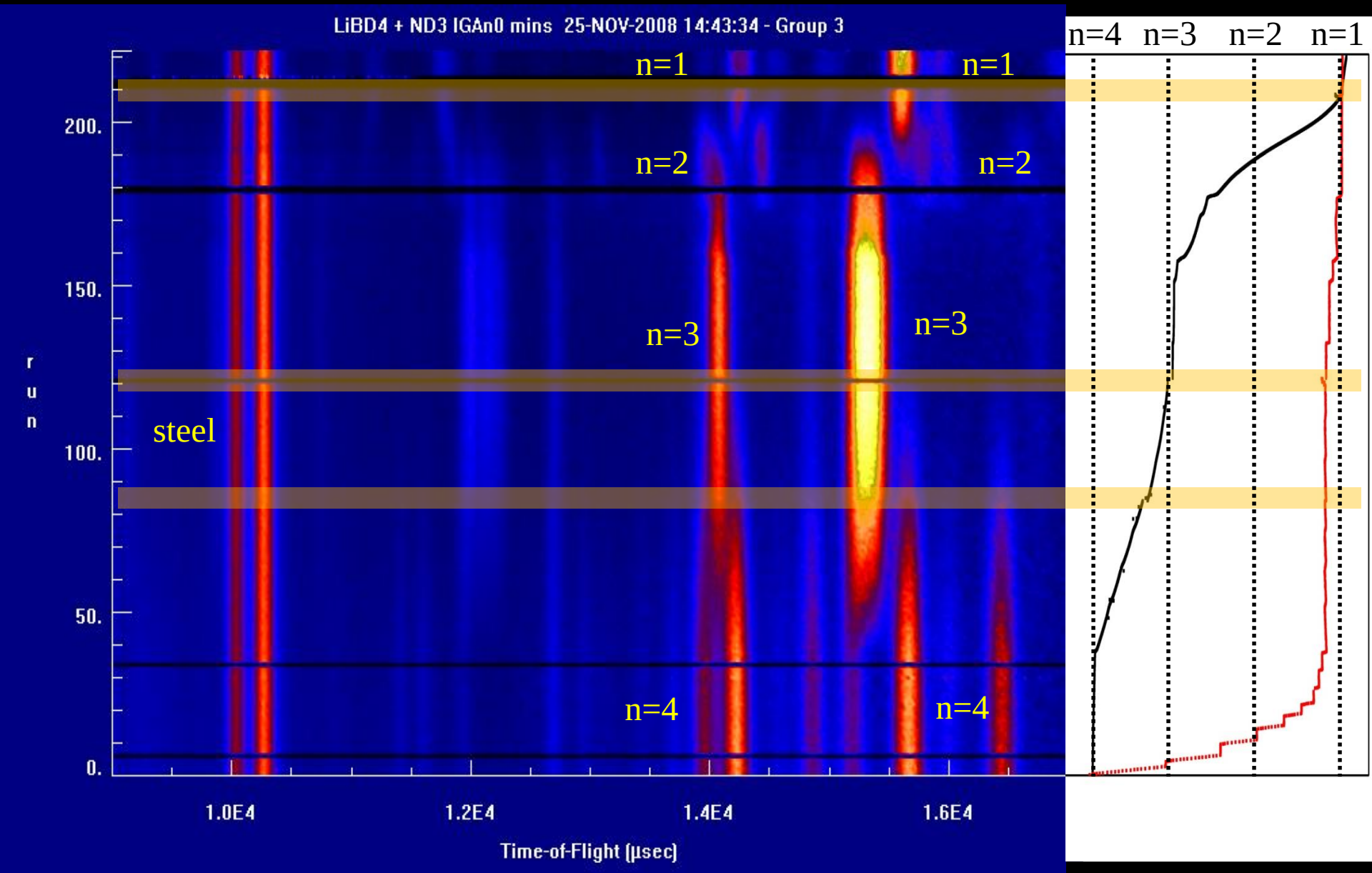
Y. Guo, G. Xia, Y. Zhu, L. Gao, X. Yu, *Chem. Commun.*, 2010, DOI: 10.1039/b924057h

Using Neutron to characterise ammines

Simultaneous thermogravimetric and diffraction studies

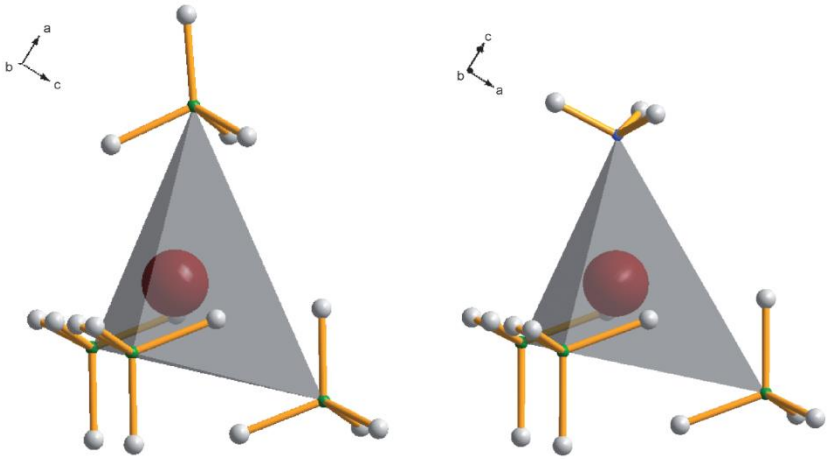


All Runs 42824-43283 $LiBD_4 + ND_3$ Desorption RT GEM bank 4 (50-74°)
(42909-42946 (inc), 42985-43099 (inc) and 43188-43271 (inc) cut)

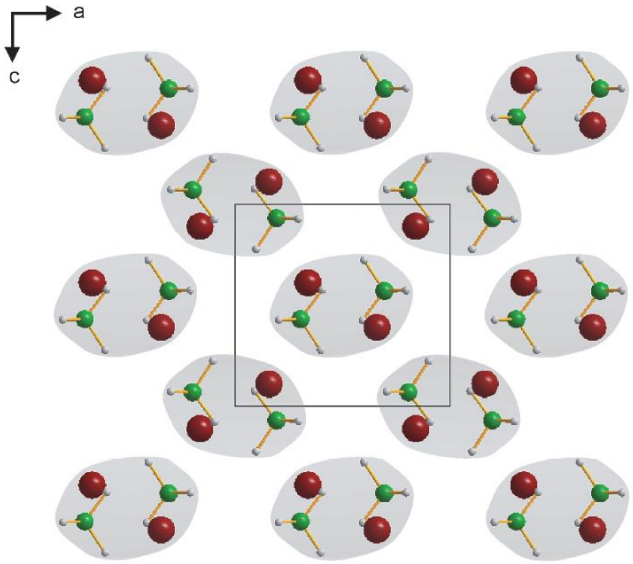


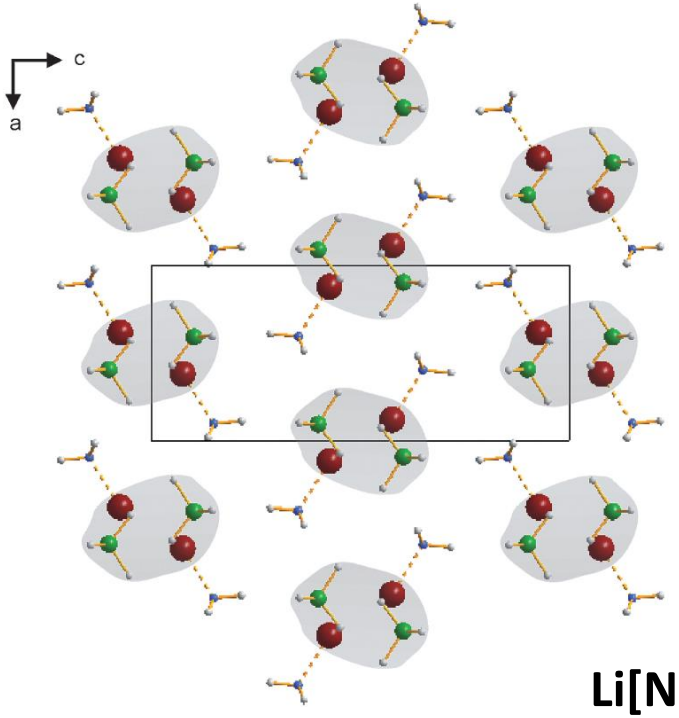
$Li[NH_3]BH_4$ - Structure

- Tetrahedral coordination about Li atoms from 3 $(BH_4)^-$ and 1 NH_3



$LiBH_4$



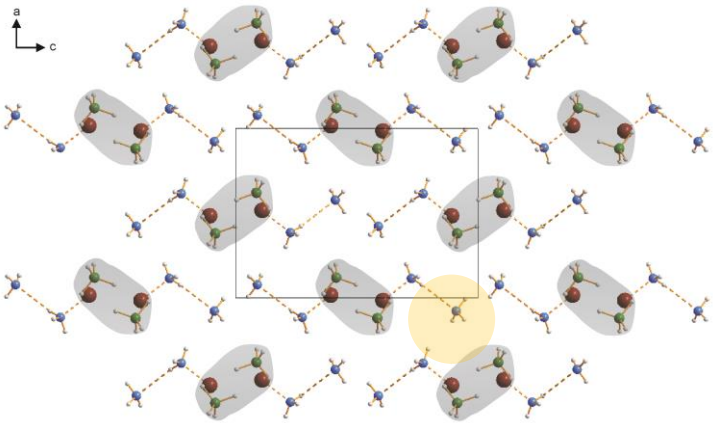


$Li[NH_3]BH_4$

S. R. Johnson, W. I. F. David, *et al*, *Chem. Asian J*. 2009, **4**, 849 – 854

$Li[NH_3]_nBH_4$

n = 2

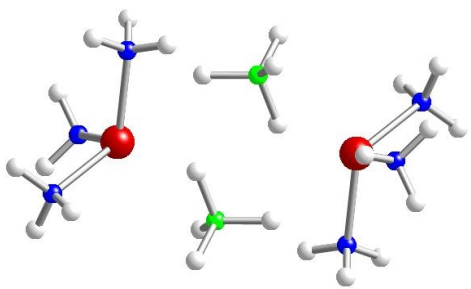


Tetrahedral Li coordination - 3 $(BH_4)^-$ and 1 NH_3

Edge-sharing chains of tetrahedra run along the b-axis

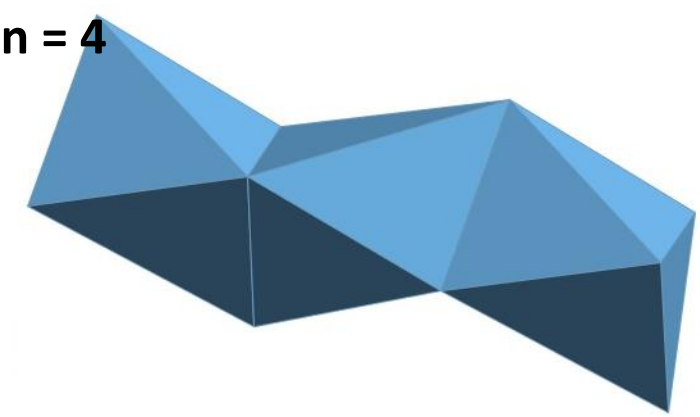
2nd NH_3 orientation s similar to solid NH_3

n = 3



Single (η^1) hydrogen bridge bonds seen for BH_4

n = 4



Layers of B and Li atoms

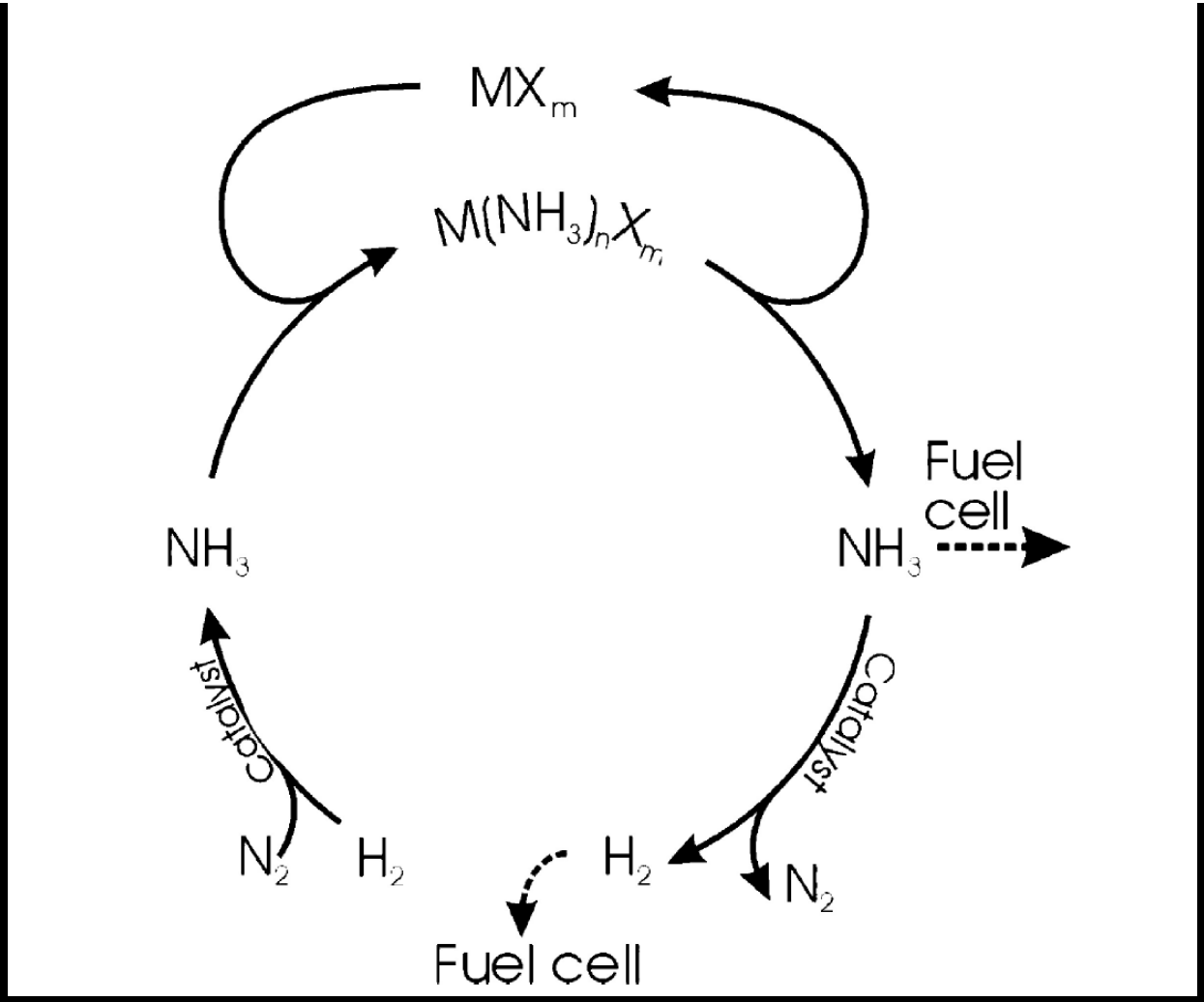
Li sits in a B_6 octahedra

Octahedra form face sharing chains along the c-axis

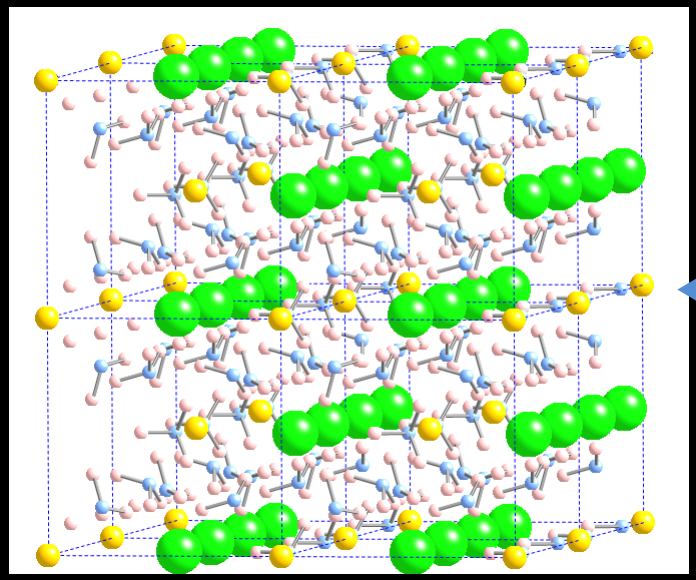
Indirect, Reversible High-Density Hydrogen Storage in Compact Metal Ammine Salts

Rasmus Z. Sørensen, Jens S. Hummelshøj, Asbjørn Klerke, Jacob Birke Reves, Tejs Vegge, Jens K. Nørskov, and Claus H. Christensen

J. Am. Chem. Soc., **2008**, 130 (27), 8660-8668• DOI: 10.1021/ja076762c • Publication Date (Web): 13 June 2008

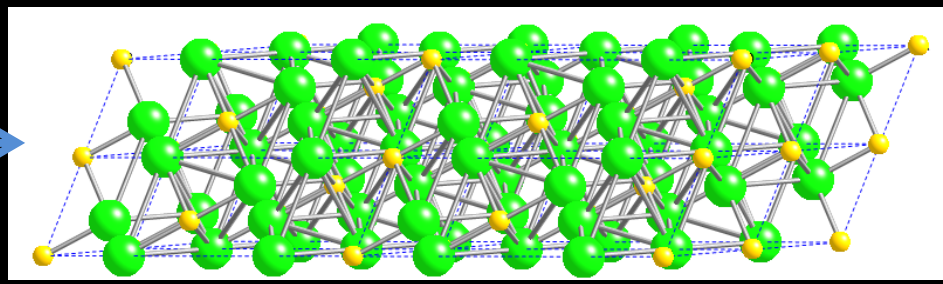


$$Mg(NH_3)_6Cl_2 \xleftrightarrow{4NH_3} Mg(NH_3)_2Cl_2 \xleftrightarrow{NH_3} Mg(NH_3)Cl_2 \xleftrightarrow{NH_3} MgCl_2$$



FM-3M

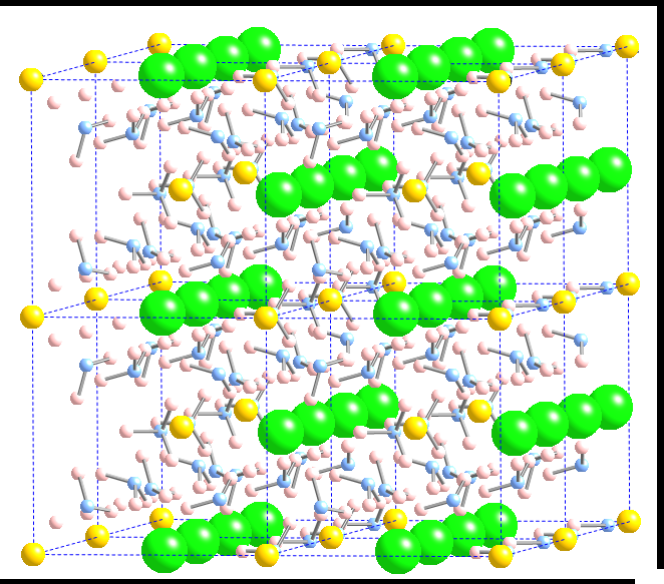
$\xleftrightarrow{-6NH_3}$



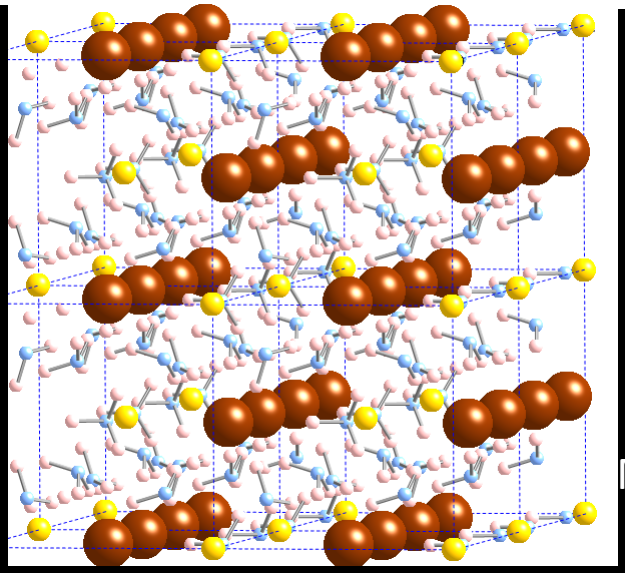
R3-MH
Chloromagnesite

J. Am. Chem. Soc., **2008**, 130 (27), 8660-8668

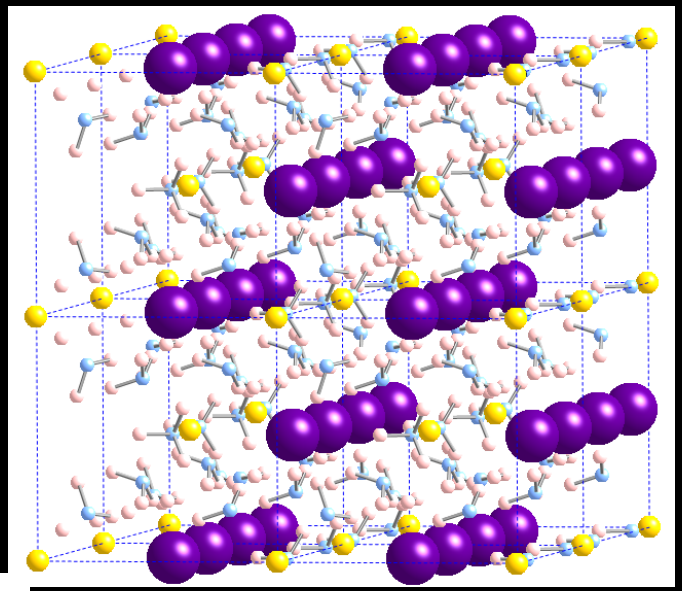
$Mg[NH_3]_6X_2$ (X = Cl, Br, I)



$Mg[NH_3]_6Cl_2$



$Mg[NH_3]_6Br_2$



$Mg[NH_3]_6I_2$

ESRF X-ray diffraction, ID31

All cubic K_2PtCl_6 structure as per $Mg[NH_3]_6Cl_2$

Structure

Compound	Cubic Lattice Parameter Å	Refinement R_{wp} %	N–H bond length Å	Mg–N bond length Å	MgNH bond angle °
$Mg(NH_3)_6Cl_2$	10.12257(6)	12.68	0.847(9)	2.158(2)	109.566(9)
$Mg(NH_3)_6Br_2$	10.40694(1)	15.22	0.71(2)	2.165(4)	109.47(2)
$Mg(NH_3)_6I_2$	10.91488(3)	14.82	0.68(2)	2.165(5)	109.35(3)

Slight increase in Mg–N bond length with increasing anion size

ESRF X-ray diffraction, ID31

NMR

Compound	Chemical Shift p.p.m.	Compound	Chemical Shift p.p.m.
$MgCl_2$	-6.9	$Mg(NH_3)_6Cl_2$	15.9
$MgBr_2$	-19.0	$Mg(NH_3)_6Br_2$	15.2
MgI_2	-81.1	$Mg(NH_3)_6I_2$	15.1

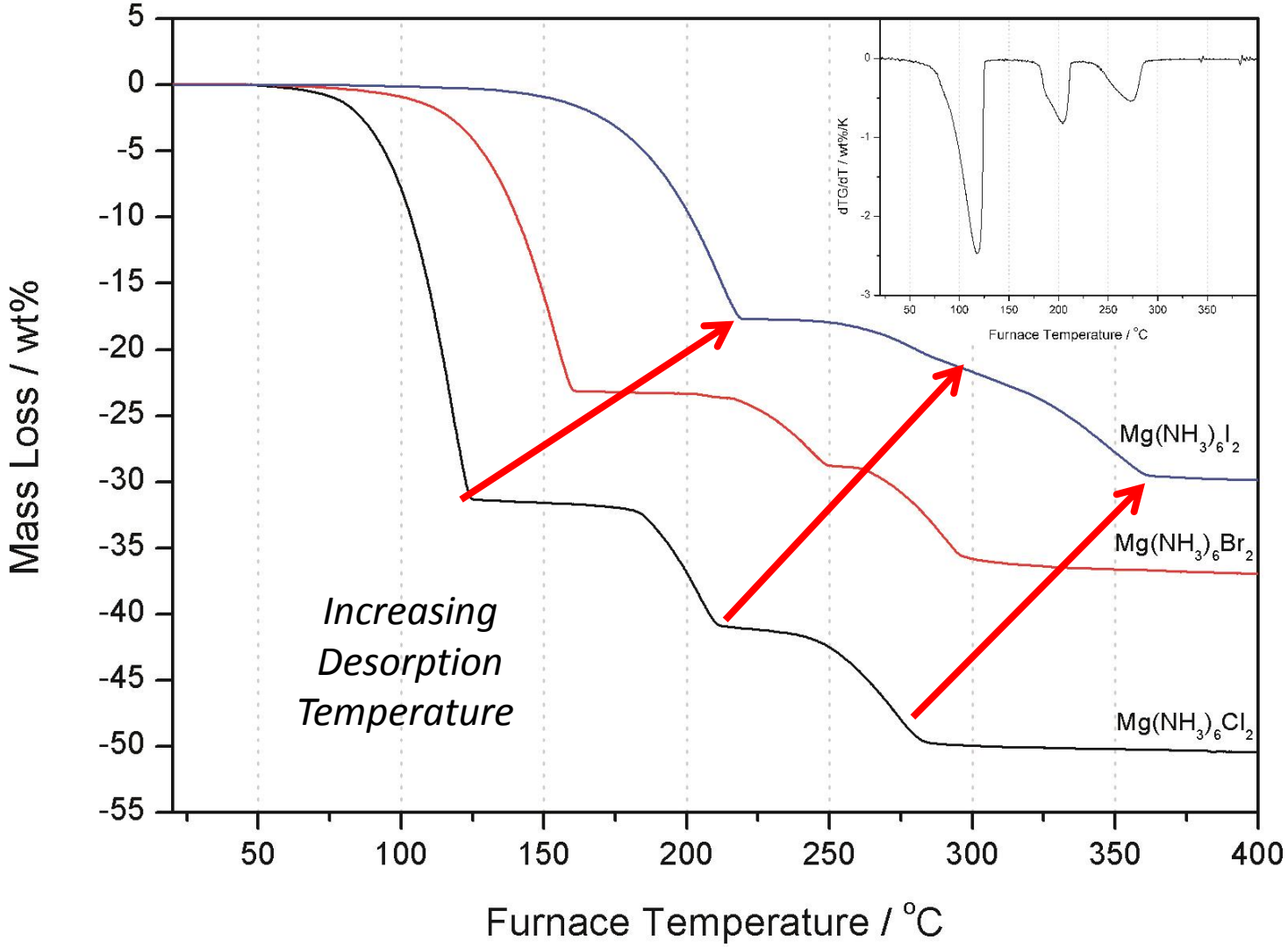
For $Mg(NH_3)_6X_2$: Decreasing Mg chemical shift with increasing atomic number

Increase in diamagnetic shielding / electron density around the Mg with the X

For MgX_2: Mg chemical shift also with increasing electron density at Mg over MgX_2

Very small change in chemical shift, which the X-ray data suggests very little change in Mg-N bonding with changing anion

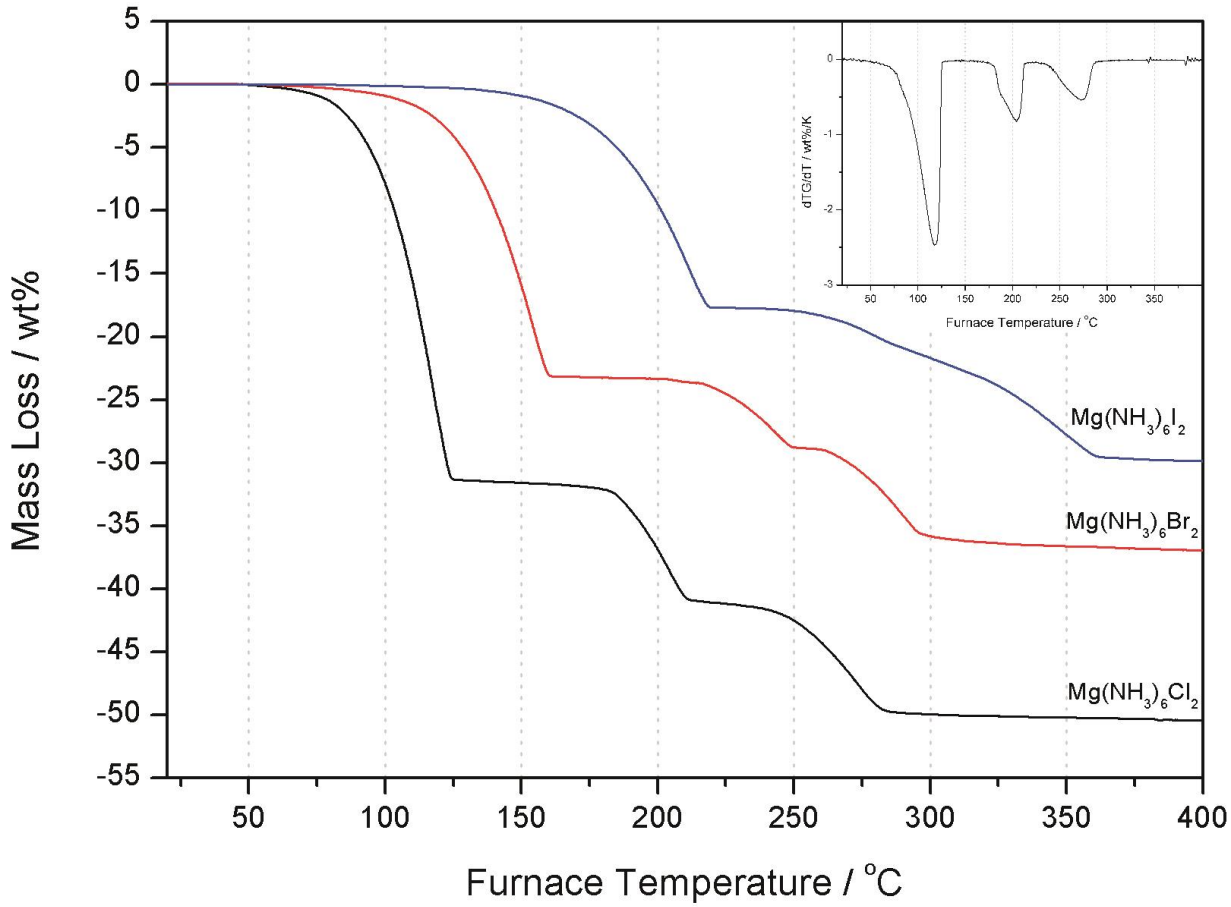
TGA


Mass Loss / wt%
Furnace Temperature / °C
Mg(NH3)6I2
Mg(NH3)6Br2
Mg(NH3)6Cl2
Increasing
Desorption
Temperature
dTG/dT / wt%/K
Furnace Temperature / °C

T_o = Onset, T_p = Peak

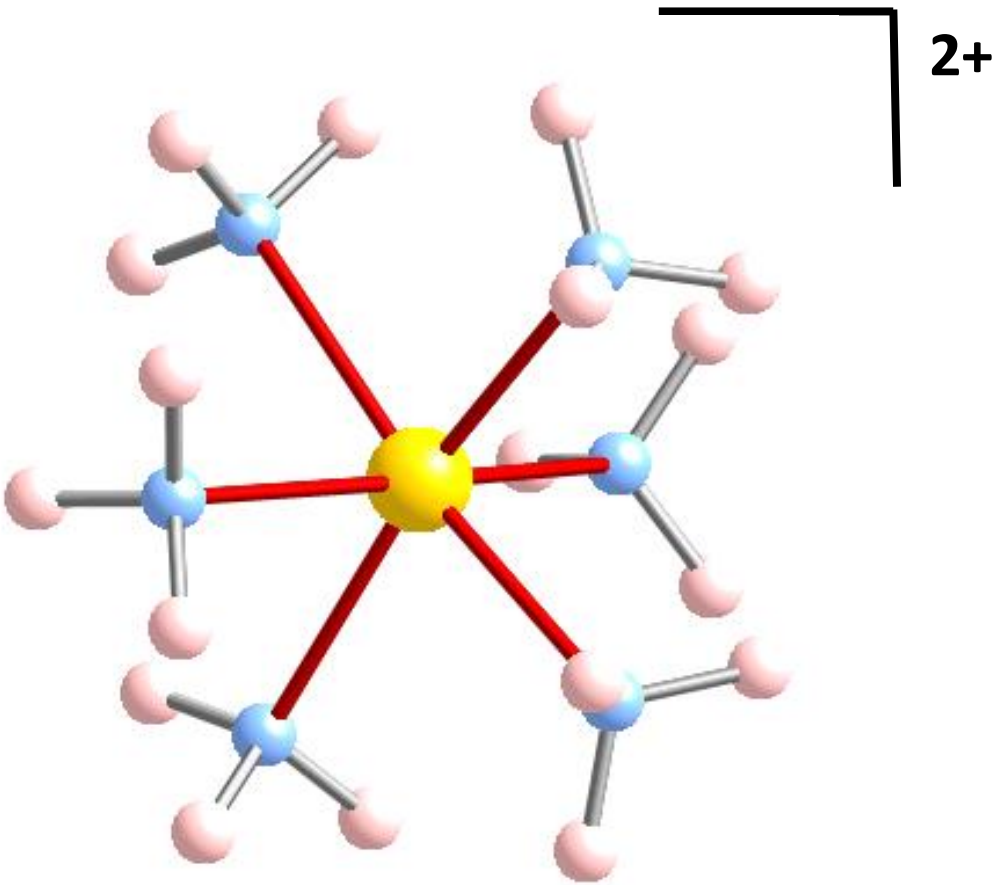
Starting Compound	Desorption Step 1			Desorption Step 2			Desorption Step 3		
	T_{1O}	T_{1P}	wt%	T_{2O}	T_{2P}	wt%	T_{3O}	T_{3P}	wt%
$Mg(NH_3)_6Cl_2$	98	117	32	187	204	10	250	274	9
$Mg(NH_3)_6Br_2$	130	155	23	223	243	6	270	292	9
$Mg(NH_3)_6I_2$	182	212	18	-	282	-	-	349	-

Increasing with anion radius



Confusing. If no change in Mg-N bonding why the difference in T_{dec}?

Assumption

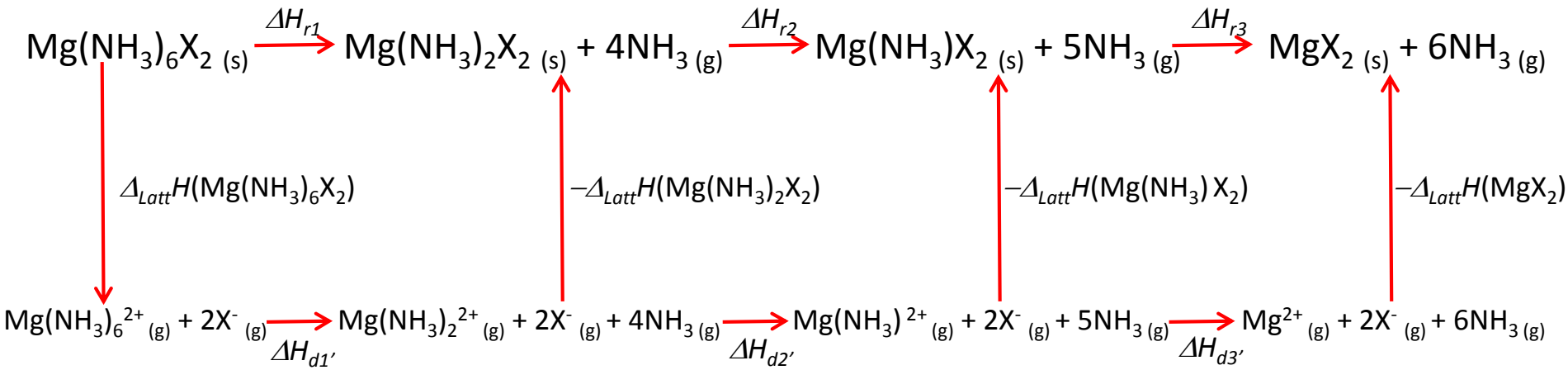


The cation is $[Mg(NH_3)_6]^{2+}$ / $[Mg(NH_3)_2]^{2+}$ / $[Mg(NH_3)]^{2+}$

rather than Mg^{2+}

Hess Cycle

Simple Ionic Model



Kapustinskii Equation

$$\Delta_{latt}H \approx \frac{\Delta|z^+|z^-|}{(r^+ + r^-)}$$

Thus the enthalpy of ammonia desorption is a more significant factor in the overall enthalpy of reaction ΔH_{r1}

Increasing anion size reduces $\Delta_{Latt}H$

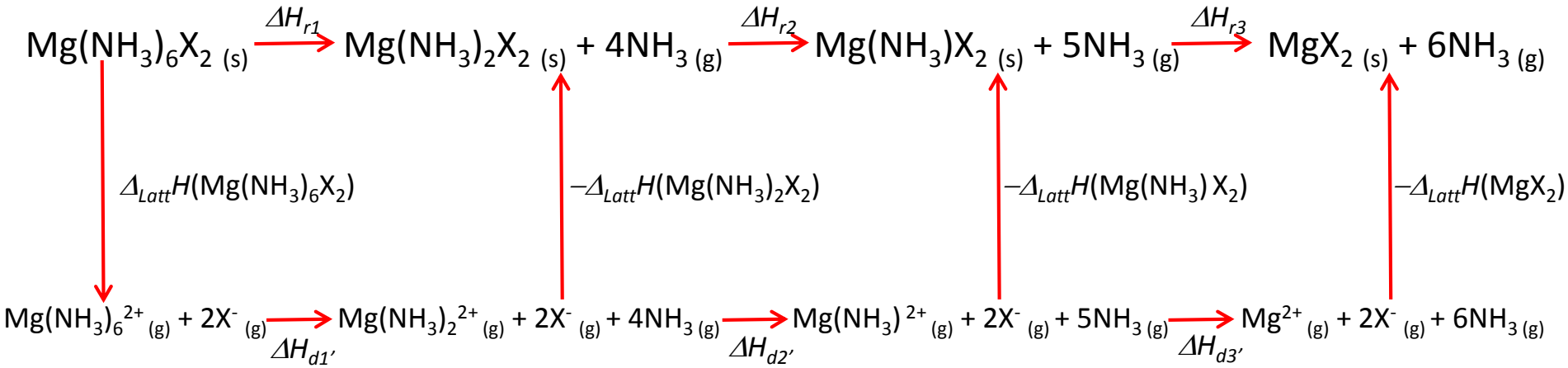
therefore, T_{dec} increases with increasing anion size

$\Delta_{Latt}H\ (Mg(NH_3)_6X_2$ - $\Delta_{Latt}H\ (Mg(NH_3)_2X_2$ is always negative (favourable)

$$T_{dec} \propto \Delta H_r \propto \frac{1}{r_{L+} + r_-} - \frac{1}{r_{S+} + r_-} + \Delta H_d$$

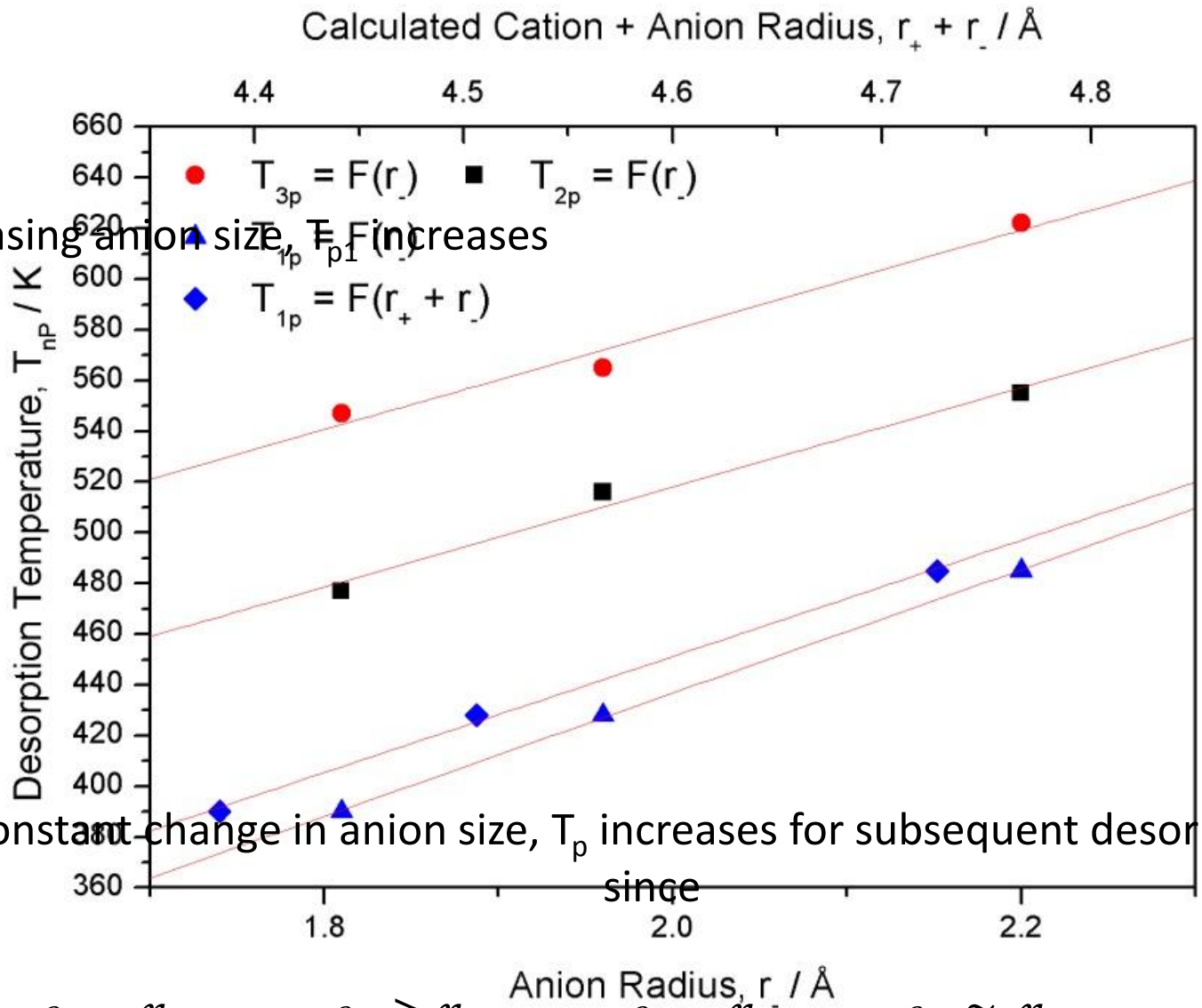
This favourable contribution decreases with increasing r^- (X radius)

Hess Cycle



Thus the enthalpy of ammonia desorption is a more significant factor in the overall enthalpy of reaction ΔH_{r1}

The enthalpy of ammonia desorption (ΔH_{d1}), which is found from our X-ray diffraction and NMR studies to be essentially independent of X



For increasing anion size, T_{p1} increases

For constant change in anion size, T_p increases for subsequent desorption steps since

$$r_{[Mg(NH_3)_6]^{2+}} - r_{[Mg(NH_3)_2]^{2+}} > r_{[Mg(NH_3)_2]^{2+}} - r_{[Mg(NH_3)]^{2+}} \approx . r_{[Mg(NH_3)_1]^{2+}} - r_{[Mg]^{2+}}$$

Why is this interesting?

Metal Ion	Ligand	Complex
Ag^{+}	2 NH_3	$Ag(NH_3)^{2+}$
Cu^{+}	2 NH_3	$Cu(NH_3)_2^{+}$
Cu^{2+}	4 NH_3	$Cu(NH_3)_4^{2+}$
Zn^{2+}	4 CN^{-}	$Zn(CN)_4^{2-}$
Hg^{2+}	4 I^{-}	HgI_4^{2-}
Co^{2+}	4 SCN^{-}	$Co(SCN)_4^{2-}$
Fe^{2+}	6 H_2O	$Fe(H_2O)_6^{2+}$
Fe^{3+}	6 H_2O	$Fe(H_2O)6^{3+}$
Fe^{2+}	6 CN^{-}	$Fe(CN)_6^{4-}$
Co^{3+}	6 NH_3	$Co(NH_3)_6^{3+}$
Ni^{2+}	6 NH_3	$Ni(NH_3)_6^{2+}$

Compound	Reversible Ammonia Content wt%	Ammonia Density gL^{-1}	Vapour Pressure at 20°C mbar	Temperature required for complete ammonia release
$Li(NH_3)BH_4$	41	296	6.7	50
$Li(NH_3)_2BH_4$	61	385	24	50
$Li(NH_3)_3BH_4$	70	526	96	50
$Li(NH_3)_4BH_4$	76	539	110	50
$Mg(NH_3)_6Cl_2$	52	641	2.0	250
$Mg(NH_3)_6(BH_4)_2$	44	357	-	75
$Ca(NH_3)_8Cl_2$	55	678	700	>100
Liquid NH_3 (-33°C)	100	682	1 017	-

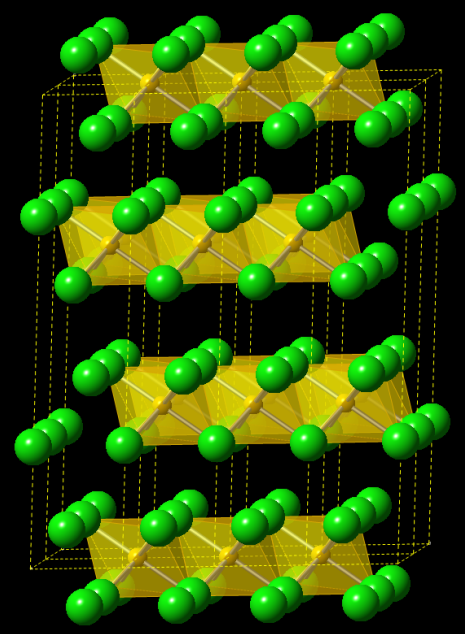
Design solid-state storage materials

Characterising Solid State Ammines

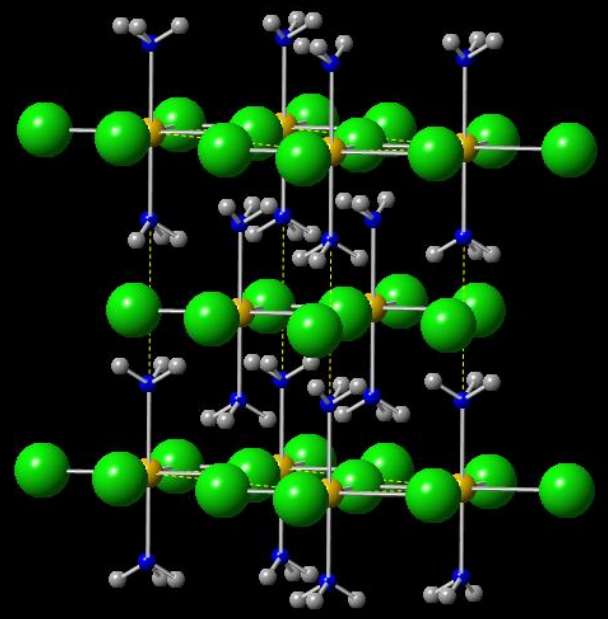
Another way to determine ammonia content?

Dielectric Constant (ε_r)

NaCl	**3**
Ammonia	**17**



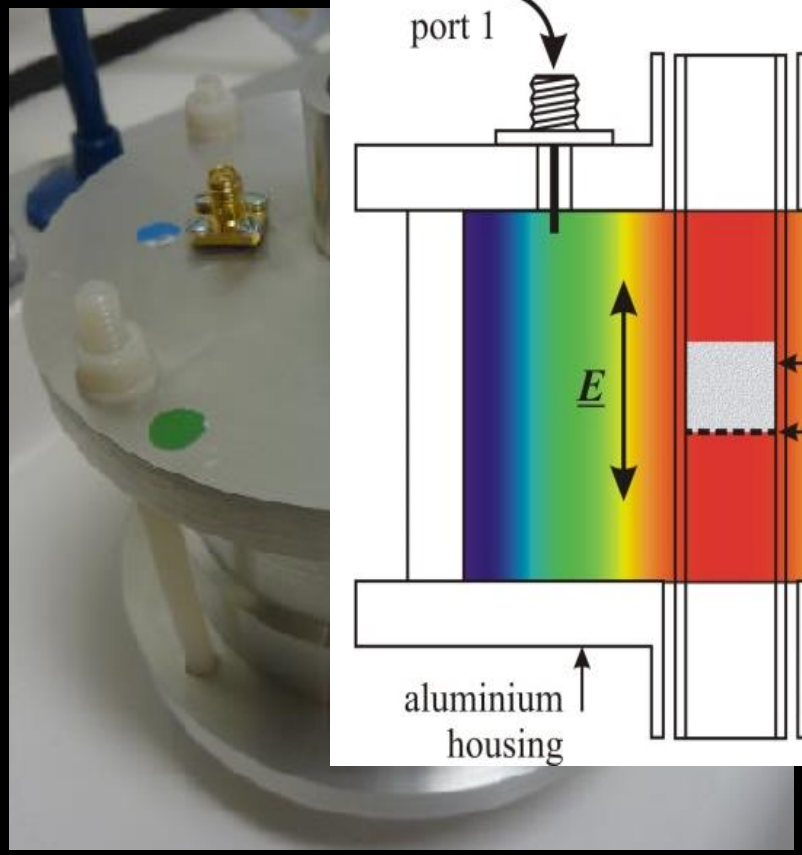
$MgCl_2$

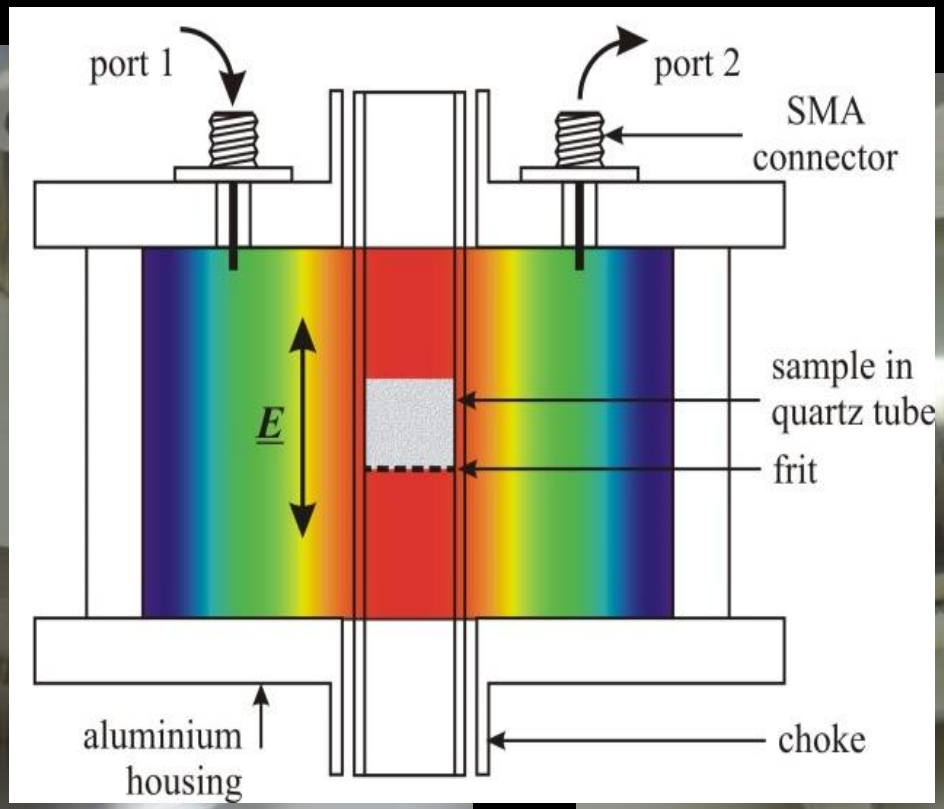


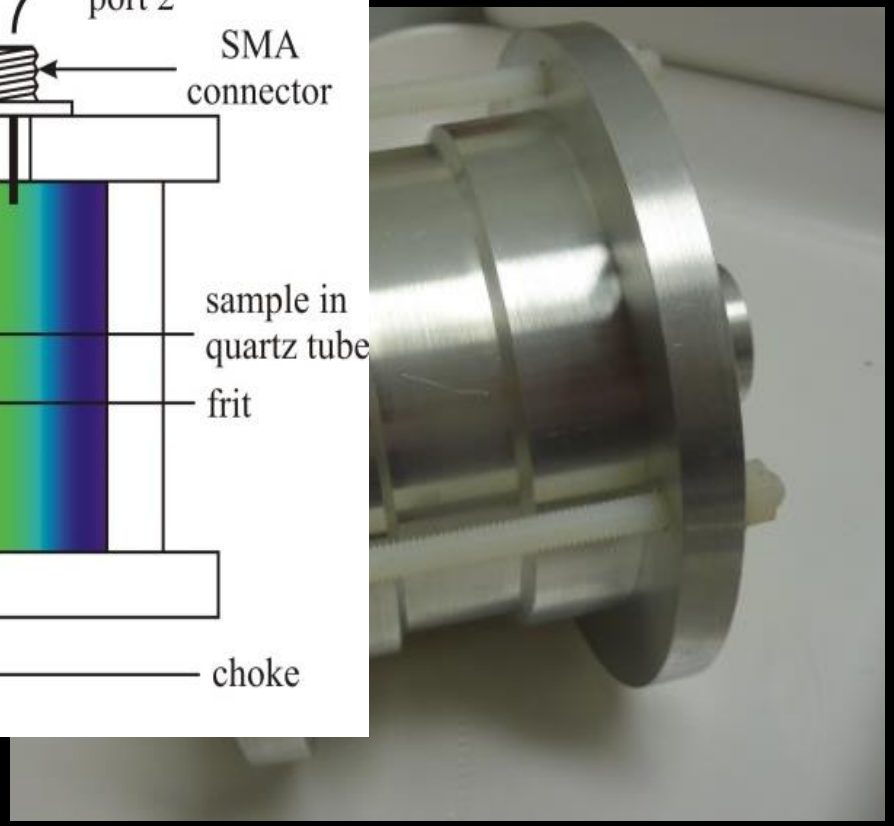
$Mg(NH_3)_2Cl_2$

Microwave dielectric resonator

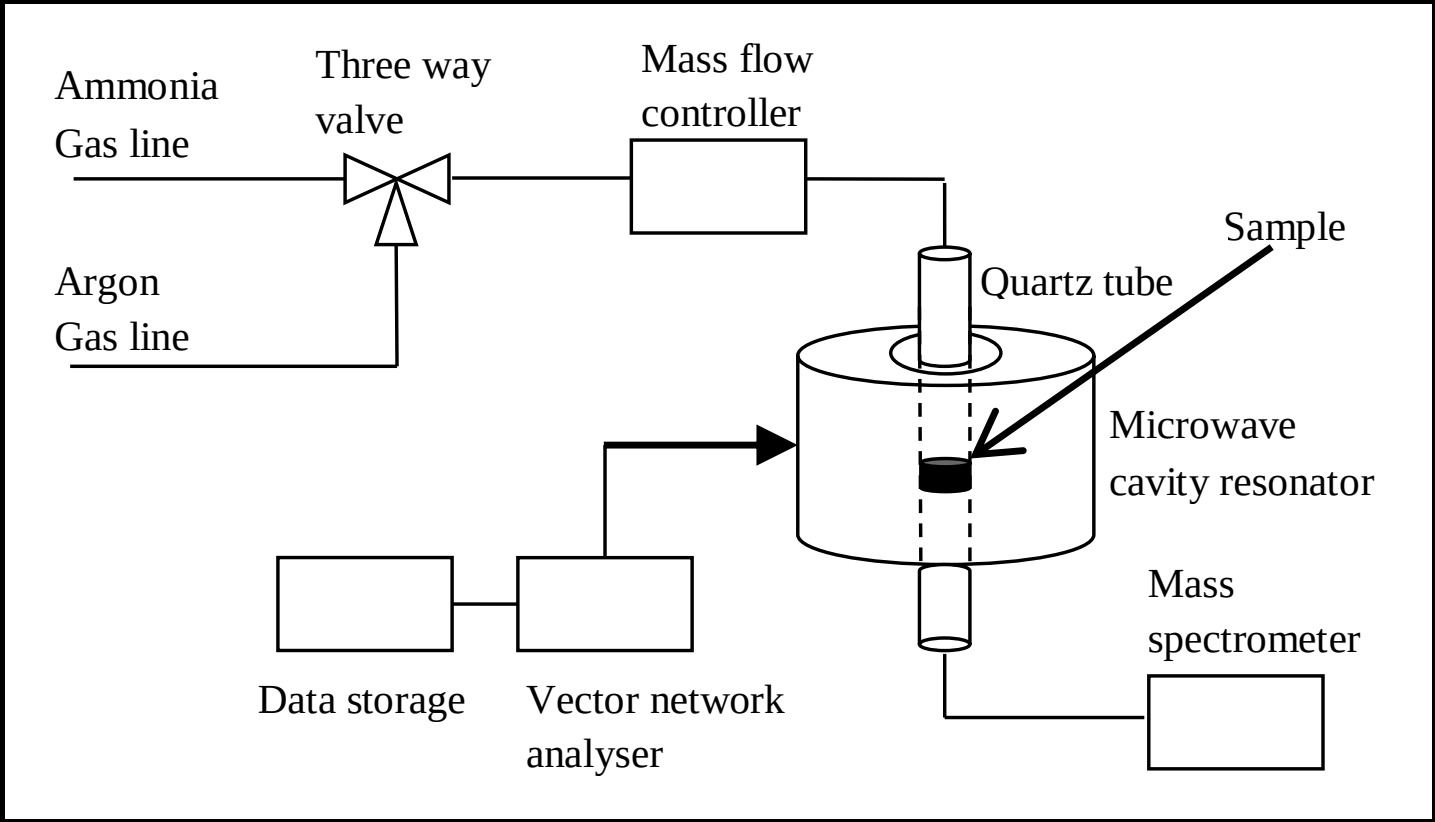
2.45 GHz, TM_{010} mode of a resonant cavity





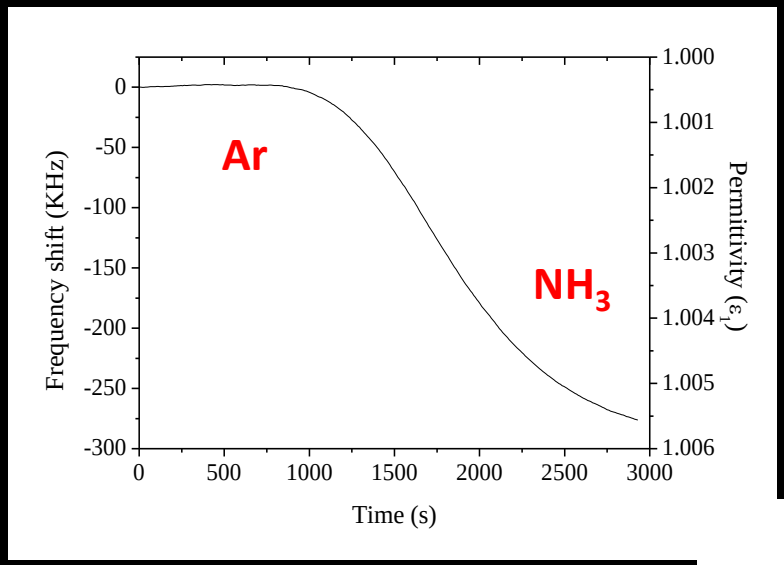


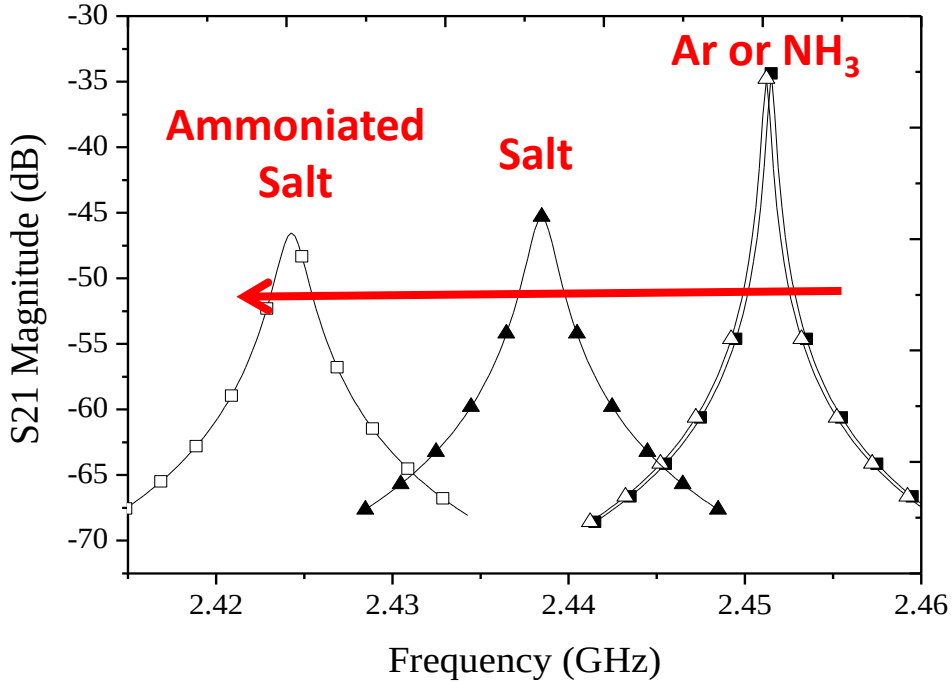
Experimental Set-Up



Experimental Set-Up

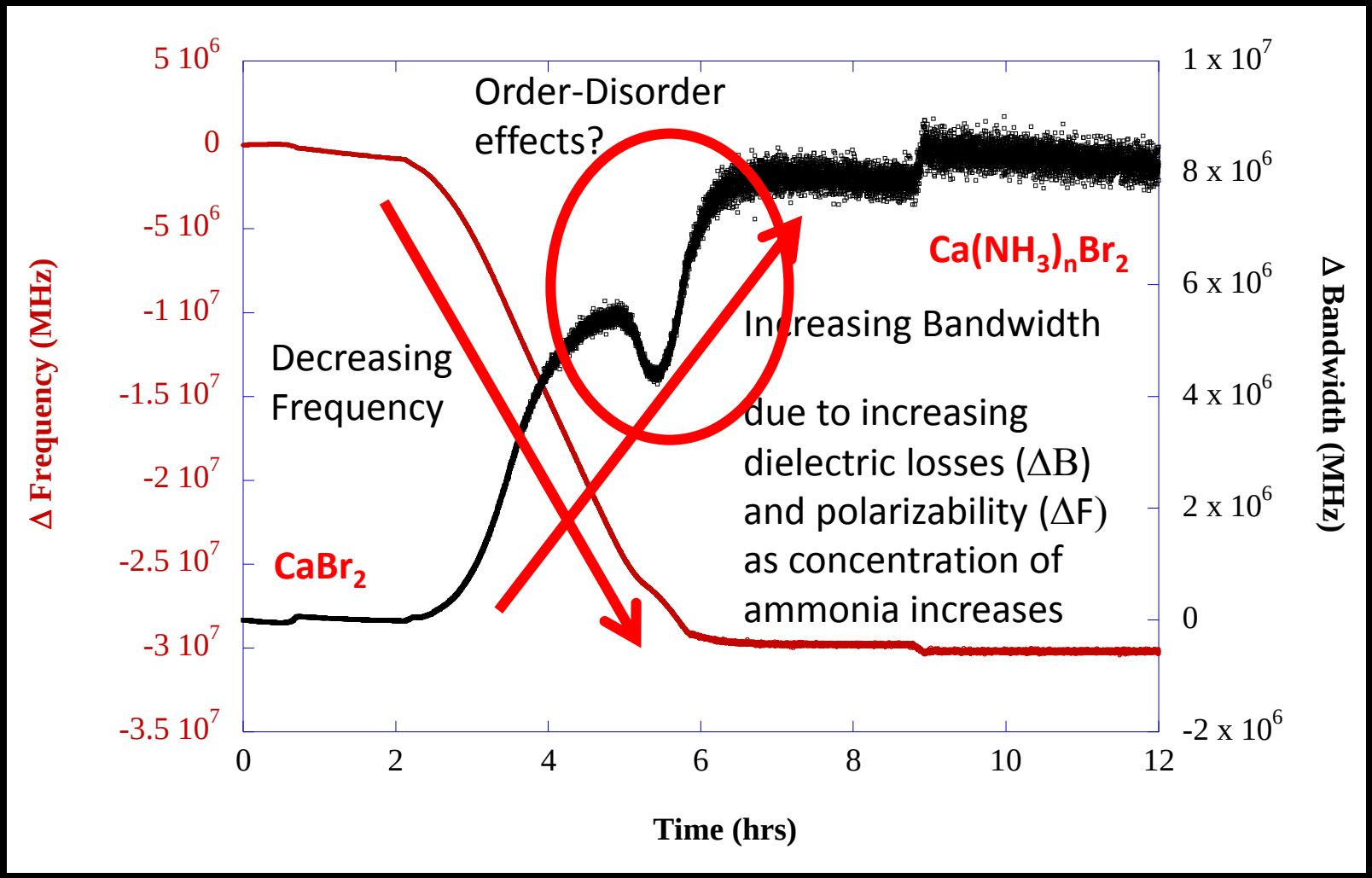
Enhanced Flow



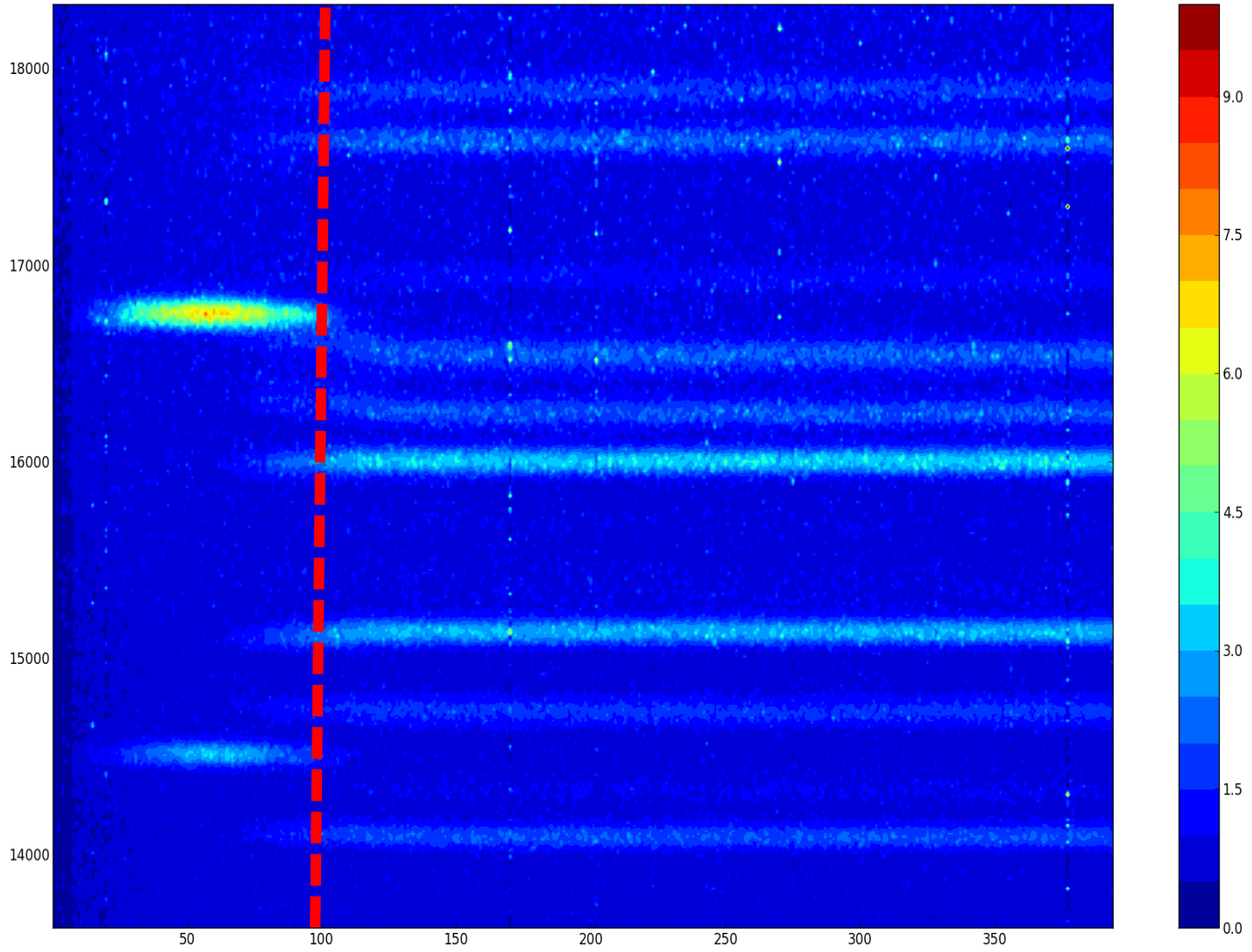


Decrease in frequency due to increasing dielectric losses (DB) and polarizability (DF) of cavity

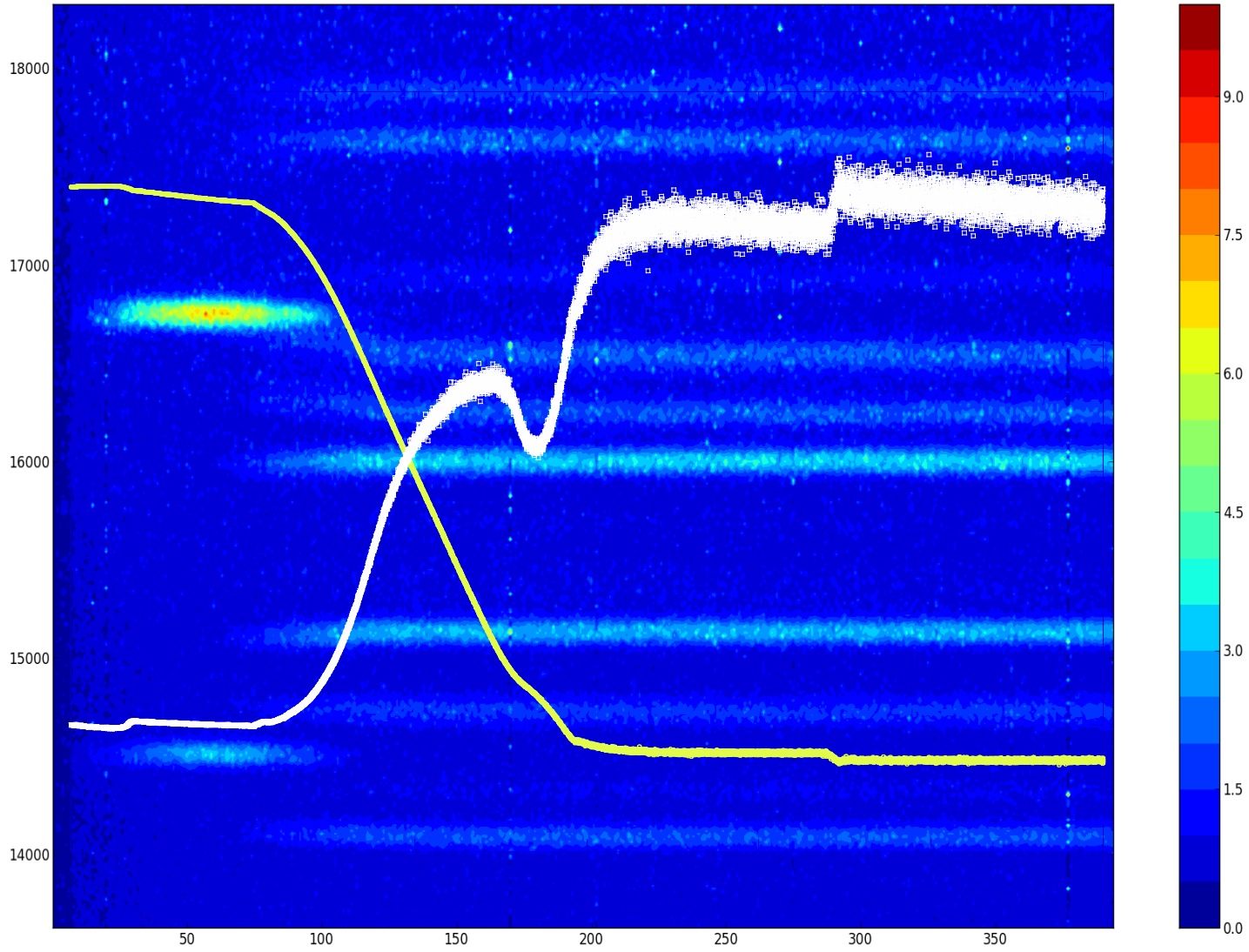
Dielectric Data



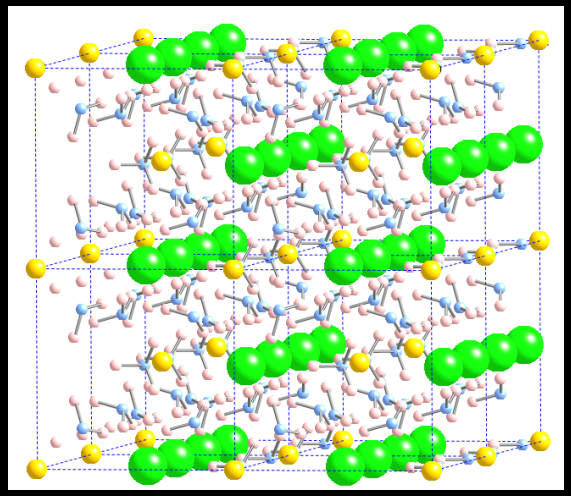
Structural Data

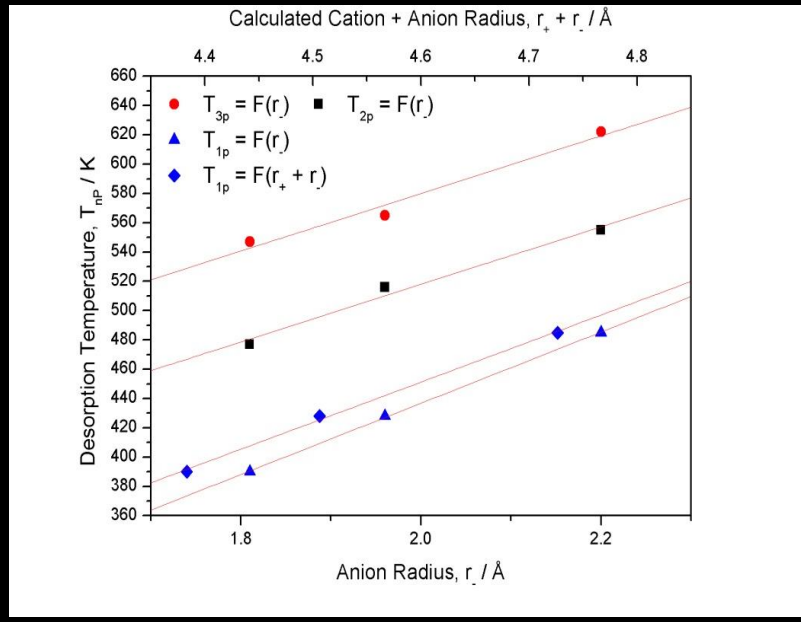


Good Correlation

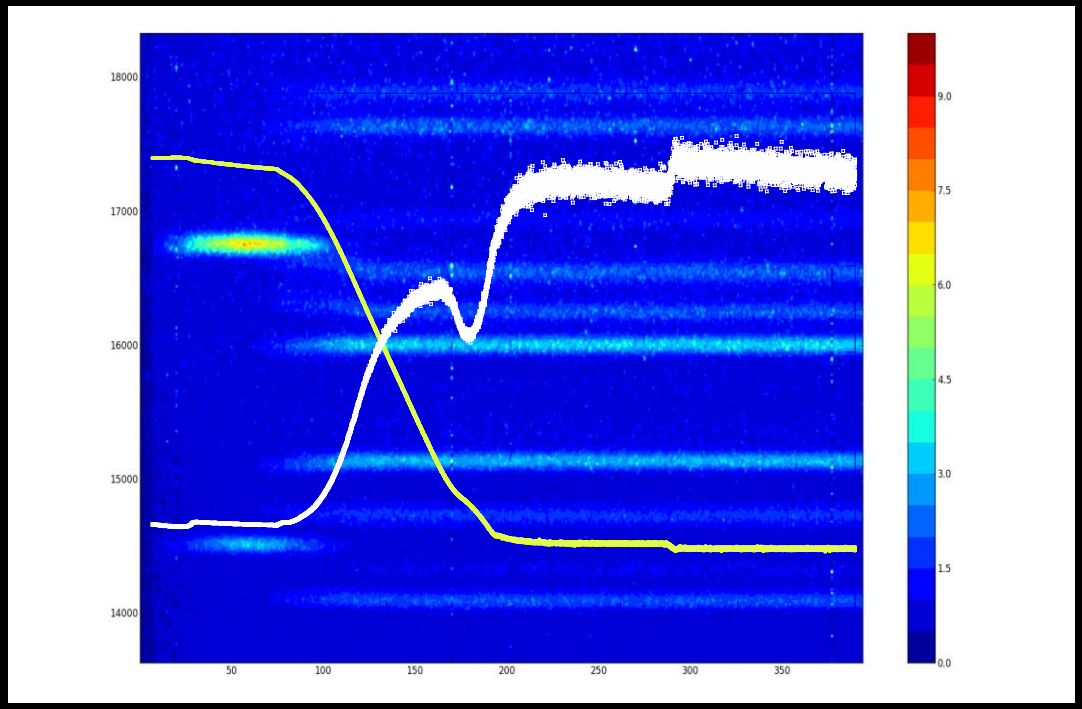


Ammines are gravimetrically and volumetrically dense hydrogen and ammonia stores





Use a simple ionic model to understand and predict the properties of ionic ammines

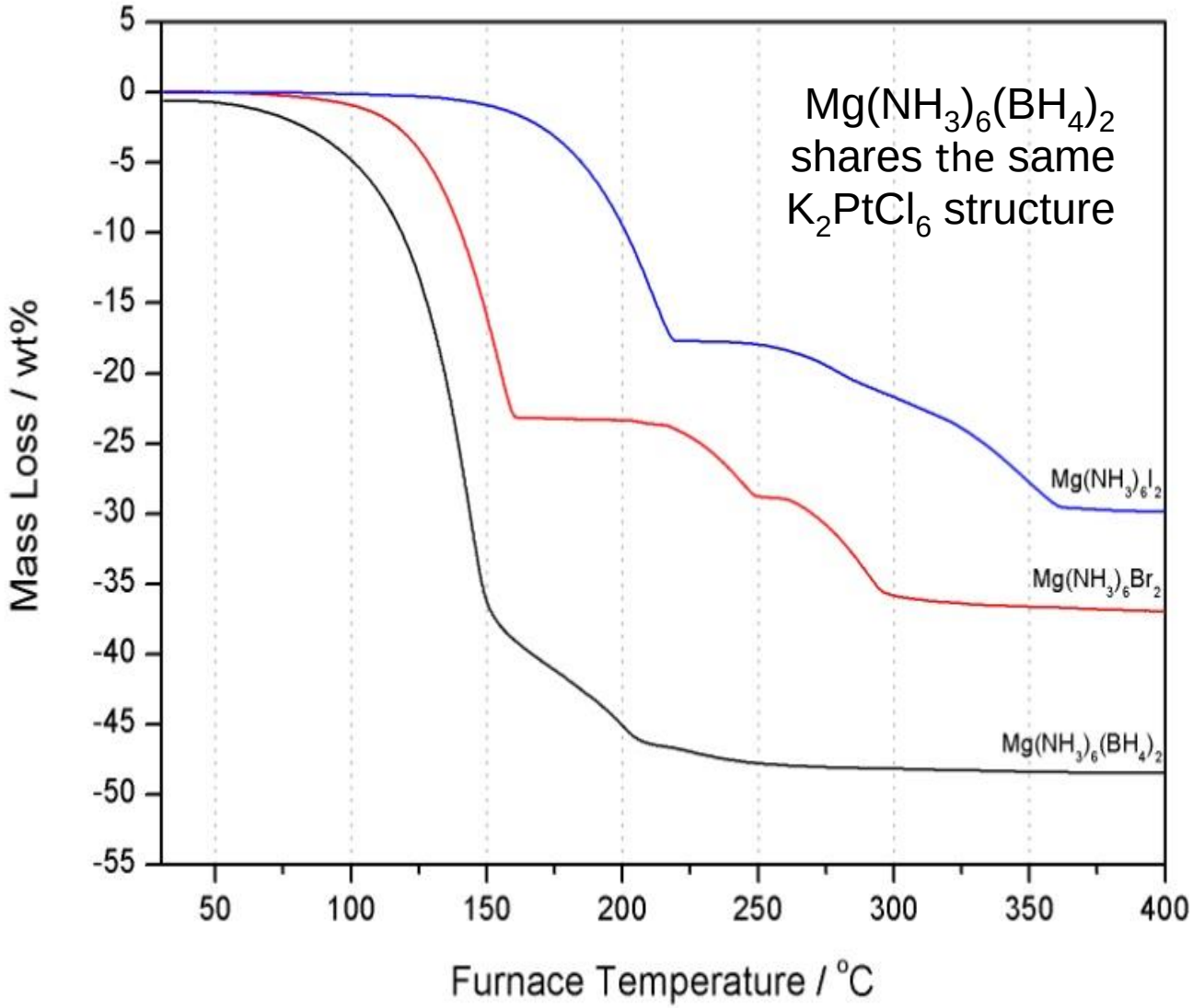


We can use simultaneous techniques to develop greater a understanding of these materials as well as developing new characterisation tools

Acknowledgements

David Royse	Oxford / STFC
Jon Hartley	Cardiff
Adrian Porch	Cardiff
Bill David	STFC / Oxford

$Mg[NH_3]_6(BH_4)_2$



Lower T_{p1}, than $Mg(NH_3)_6Br_2$ (2.03 for BH_4^- *cf.* 1.96 for Br^-)

dihydrogen bonding in the intermediate $Mg(NH_3)_2(BH_4)_2$, as proposed in *Soloveichik Inorg. Chem.*, 2008, **47** (10)

Simultaneous neutron diffraction

$CaBr_2$

$$CaBr_2 + NH_3 \rightleftharpoons CaBr_2 \cdot NH_3 \quad (5)$$

$$CaBr_2 \cdot NH_3 + NH_3 \rightleftharpoons CaBr_2 \cdot 2NH_3 \quad (6)$$

$$CaBr_2 \cdot 2NH_3 + 4NH_3 \rightleftharpoons CaBr_2 \cdot 6NH_3 \quad (7)$$

$$CaBr_2 \cdot 6NH_3 + 2NH_3 \rightleftharpoons CaBr_2 \cdot 8NH_3 \quad (8)$$