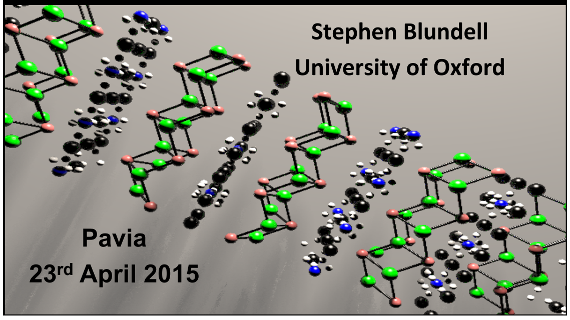
How to build a superconductor



Stephen Blundell
University of Oxford

Pavia
23rd April 2015

How to build a superconductor

Thanks to:

Francesca Foronda, Jack Wright, Johannes Möller, Franz Lang, Ben Williams *(Oxford Physics)*

Simon Clarke, Daniel Woodruff, Simon Cassidy, Genevieve Allcroft, Amber Thompson, Michael Pitcher, Dinah Parker, Dave Free, Matthew Burrard-Lucas, Stefan Sedlmaier *(Oxford Chemistry)*

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Roustem Khasanov, Alex Maisuradze *(PSI)*

Outline

① **Introduction**
② **Intercalation** – adding new layers
③ Molecular intercalated iron-based superconductor: $\mathbf{Li_x(NH_2)_y(NH_3)_{1-y}Fe_2Se_2}$
④ Other molecular intercalated iron-based superconductors
⑤ $\mathbf{Li_{1-x}Fe_x(OH)Fe_{1-y}Se}$ – a continuously tunable superconductor

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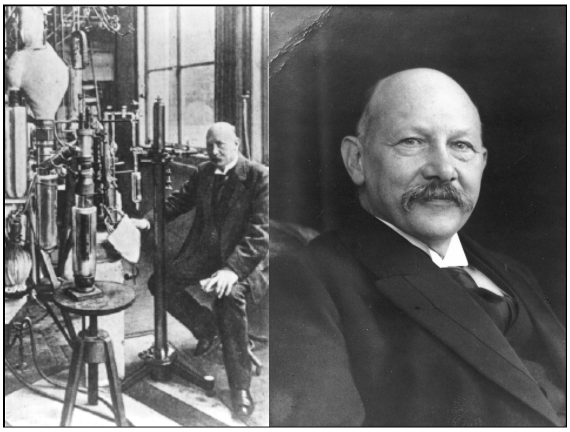
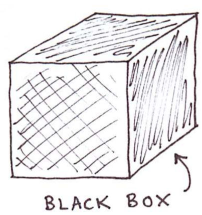


Thought experiment



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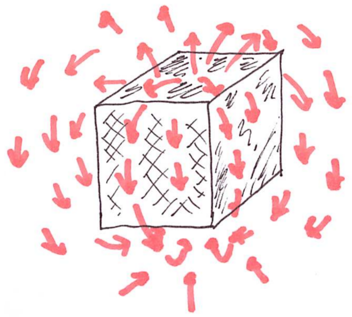

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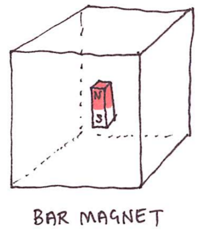
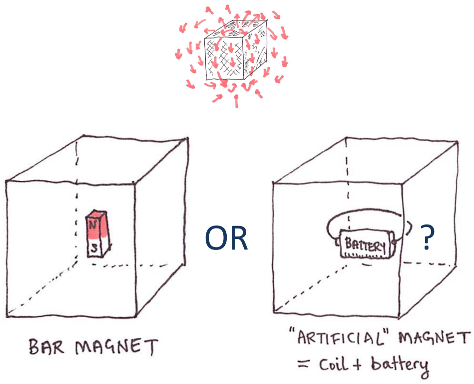
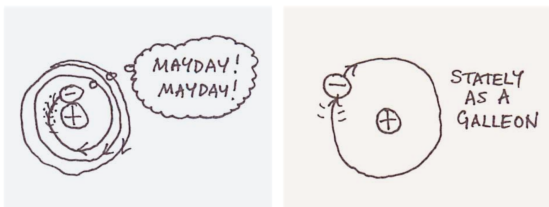
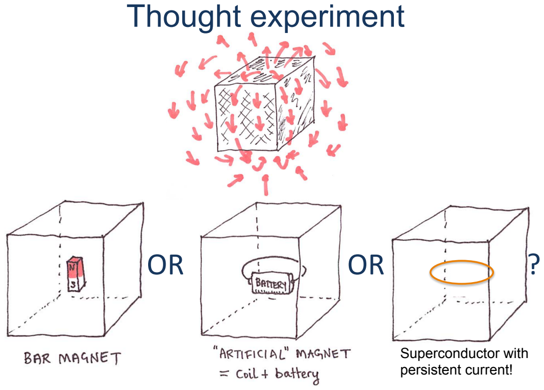




The atom



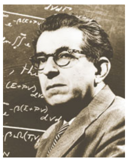
Thought experiment



Our house was a two storey house. I was in the kitchen cooking and suddenly the upstairs door was opened by Fritz. `Edith, Edith come, we have it. Come up, we have it.' And maybe the wind closed the door. I do not know what had happened upstairs. I left everything, ran up and, then, the door was opened in my face. On my forehead I had a bruise for a week. Fritz said `The equations are established. We have the solution. We can explain it.'

Edith London

London equations



Fritz London: superconductivity due to macroscopic quantum phenomenon

LRO of momentum vector

⇒ condensation in p-space

Rigidity of superconducting wave function ψ responsible for diamagnetism.

London equation: condense into $\vec{p} = 0$ state

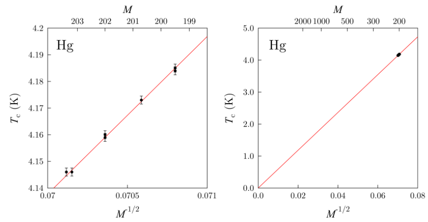
$$\hat{\vec{p}} = -i\hbar\vec{\nabla} = m\vec{v} + q\vec{A} = 0$$

$$\Rightarrow \vec{v} = -\frac{q\vec{A}}{m} \qquad (\vec{J} = nq\vec{v})$$

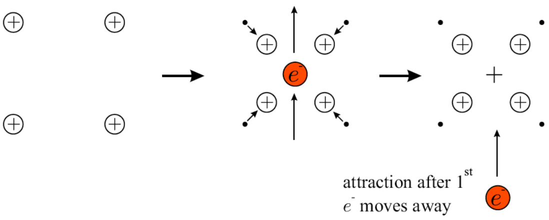
$$\Rightarrow \boxed{\vec{J} = -\frac{nq^2}{m}\vec{A}}$$ London equation

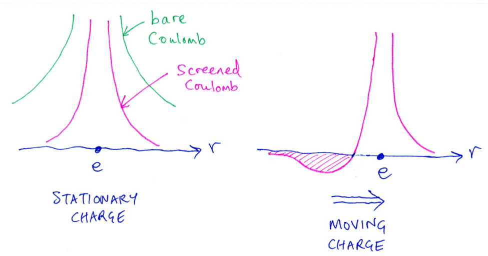
The isotope effect

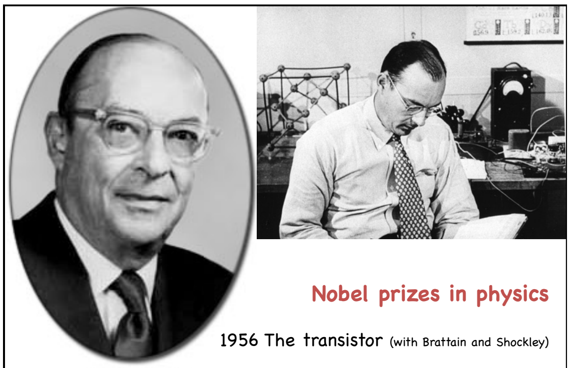
The transition temperature $T_c \propto M^{-1/2}$ where M is the mass of the isotope.



This is very good evidence for the role of *phonons* in superconductivity.





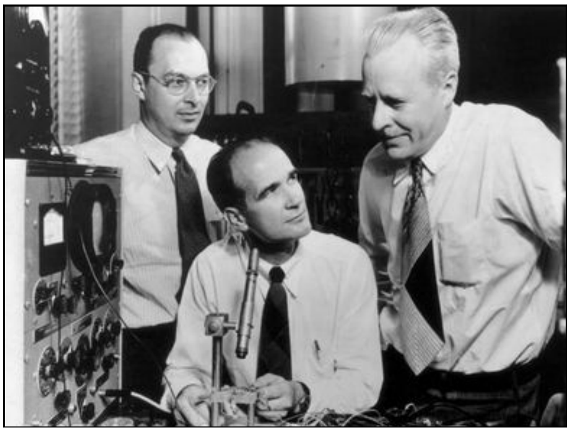


Nobel prizes in physics

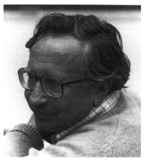
1956 The transistor (with Brattain and Shockley)

1972 BCS theory (with Cooper and Schrieffer)

John Bardeen (1908-1991)



How to discover new superconductors



Bernd Matthias (1918-1980)

Igor Mazin

Rules for discovering superconductors

1. High symmetry good, cubic best
2. Need a large DOS at E_F
3. Stay away from oxides
4. Stay away from magnetism
5. Stay away from insulators
6. Stay away from theorists

New rules for discovering superconductors

1. Layered structure good
2. Carrier density not too high
3. Oxides, arsenides fine
4. Magnetism essential
5. Insulators OK, 3d metal ions are good
6. Stay away from theorists

Superconducting elements known in 1920

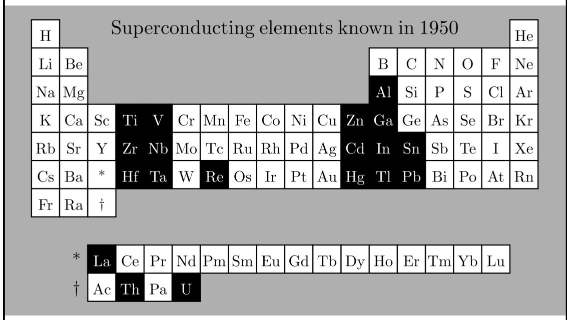
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	**Sn**	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	**Hg**	**Tl**	**Pb**	Bi	Po	At	Rn
Fr	Ra	†															

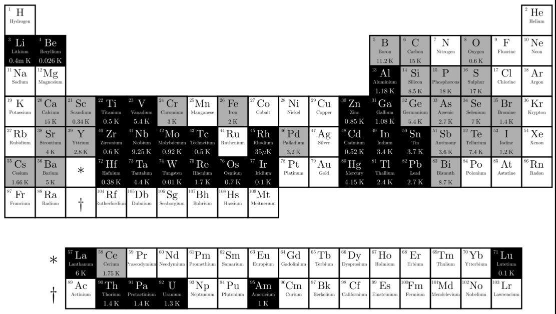
*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†	Ac	Th	Pa	U											

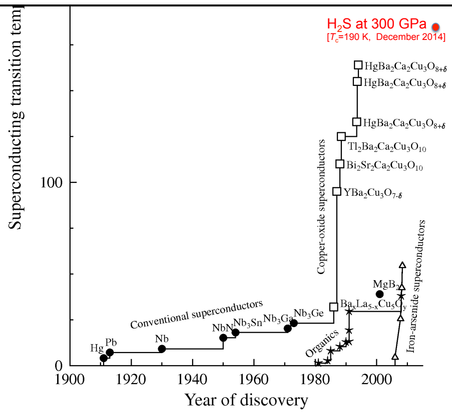
Superconducting elements known in 1930

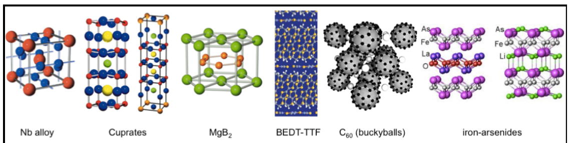
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	**Ti**	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	**Ga**	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	**Nb**	Mo	Tc	Ru	Rh	Pd	Ag	Cd	**In**	**Sn**	Sb	Te	I	Xe
Cs	Ba	*	Hf	**Ta**	W	Re	Os	Ir	Pt	Au	**Hg**	**Tl**	**Pb**	Bi	Po	At	Rn
Fr	Ra	†															

*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†	Ac	**Th**	Pa	U											

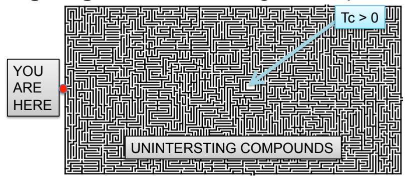






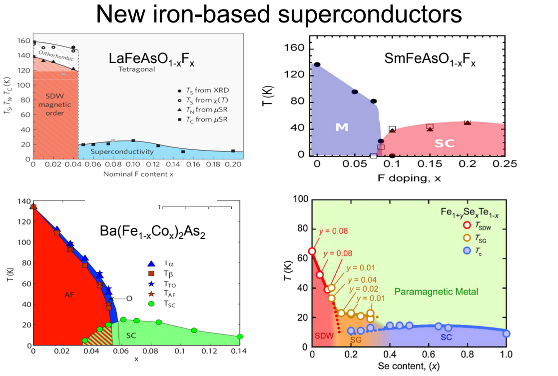


Navigating the maze: finding new superconductors



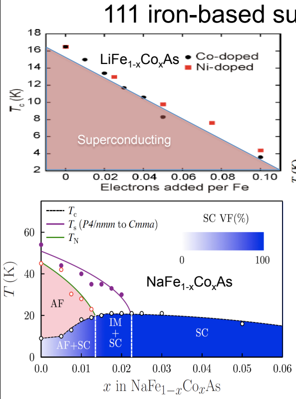
- It's worse than this! Chemical space is high-dimensional.
- If we're honest, most big discoveries have been by luck.
- Once you make a discovery, we have strategies to optimise.

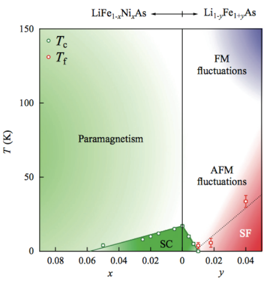
New iron-based superconductors



Nature Mat. **8**, 305 (2009); 8, 310 (2009); PRB **80**, 052503 (2009); **79**, 144523 (2009); JPSJ **79**, 113702 (2010)

111 iron-based superconductors





M. J. Pitcher et al. JACS **132**, 10467 (2010);
D. R. Parker et al. PRL **104**, 057007 (2010);
J. D. Wright et al. PRB **85** 054503 (2012);
J. D. Wright et al., PRB **88**, 060401 (2013)

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Intercalation

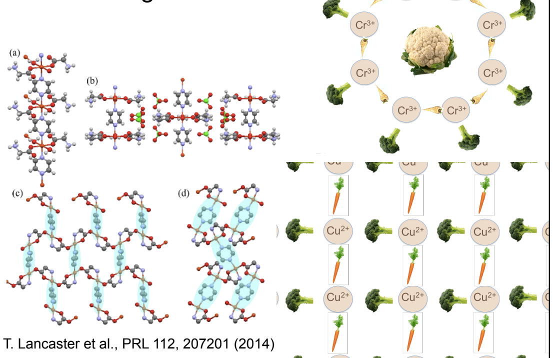
inter = between
calare = to proclaim solemnly (same root as *calendar*)

Insert days into the calendar to bring the current reckoning of time into natural harmony (first recorded use, 1614)

1844, Ralph Waldo Emerson, Essays: Second Series, ch. 2:
"[T]is wonderful where or when we ever got anything of this which we call wisdom, poetry, virtue. We never got it on any dated calendar day. Some heavenly days must have been **intercalated** somewhere."

Used for chemistry first in 1960 (F. N. Lewis)

Molecular/organic architectures



T. Lancaster et al., PRL 112, 207201 (2014)

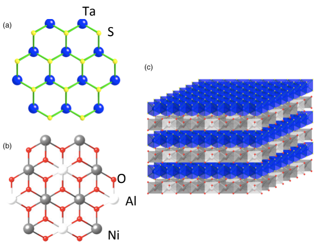
Molecular/organic architectures

useful for superconductivity?

Coexistence of superconductivity and magnetism by chemical design and nanosheet assembly

superconducting
TaS_2

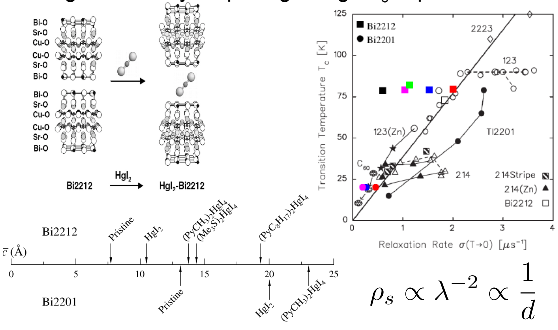
magnetic
$M(OH)_2$



$[Ni_{0.66}Fe_{0.33}(OH)_2][TaS_2]$ T_c (super) ~ 4 K T_N (magnetic) ~ 16 K

E. Coronado, C. Martí-Gastaldo, E. Navarro-Moratalla, A. Ribera, S. J. Blundell and P. J. Baker, Nature Chemistry **2**, 1031 (2010)

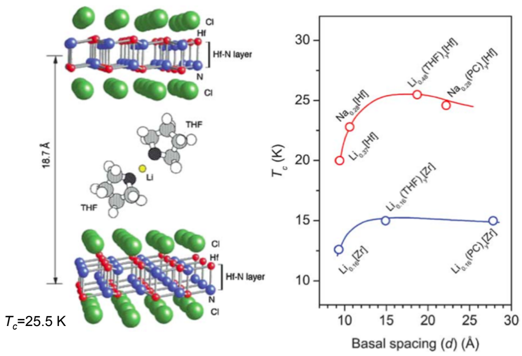
Tuning the interlayer spacing in high T_c superconductors



$$\rho_s \propto \lambda^{-2} \propto \frac{1}{d}$$

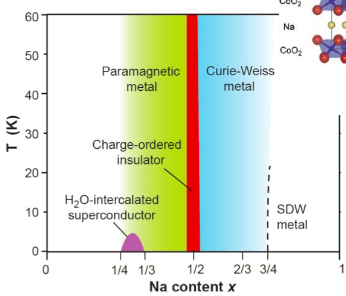
P.J. Baker, T. Lancaster, S.J. Blundell, F.L. Pratt, M.L. Brooks and S.-J. Kwon, Phys. Rev. Lett. **102**, 087002 (2009);
J.-H. Choy, S. J. Kwon, and K. S. Park, Science **280**, 1589 (1998).

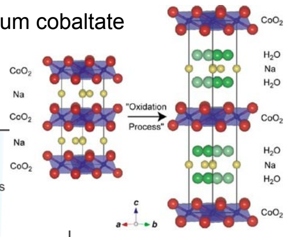
Intercalation of $Li(THF)_2$ in HfNCl



S. Yamanaka et al., Nature **392**, 380 (1998); S. Yamanaka, J. Mater. Chem. **20**, 2922 (2010)

"Just add water" – sodium cobaltate





$Na_{0.3}CoO_2 \cdot 1.3H_2O$

T_c~5 K

K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki. Nature **422**, 53 (2003).

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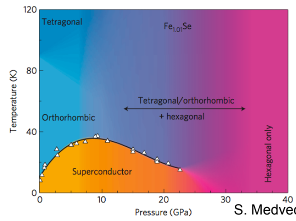
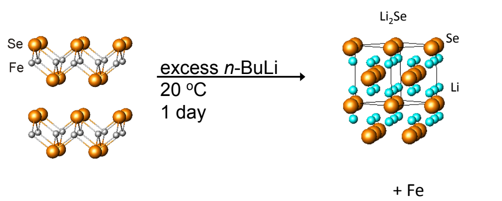
$Fe_{1+\delta}Se$

- $Fe_{1.01}Se$ (T_c~8.5 K) loses superconductivity by additional interstitial Fe
- As for LiFeAs, (i) superconductivity occurs close to stoichiometric composition (Fe^{2+}) and (ii) FeQ_4 (Q=As,Se) tetrahedra highly compressed.
- Pressure: T_c~37 K at 7 GPa
- No magnetic phase transition
- Very small Fermi surface pockets



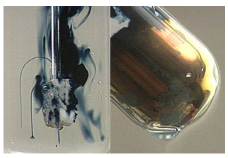
S. Medvedev et al. Nature Materials 8, 630 (2009)

Soft chemistry with FeSe

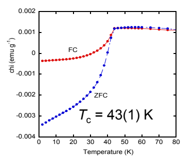


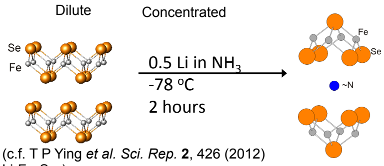
Reductive intercalation results in extrusion of Fe (as in Cu oxide chalcogenides)

Alkali metals in ammonia



Dilute Concentrated





Lab powder X-ray *I4/mmm*

a = 3.8249(2) Å (1.4% larger than FeSe)

c = 16.527(1) Å (c.f. *c* = 13.8811(5) Å in $K_{0.8}Fe_{1.6}Se_2$)

(c.f. T P Ying *et al. Sci. Rep.* **2**, 426 (2012) $Li_xFe_2Se_2$)

Initial structural analysis

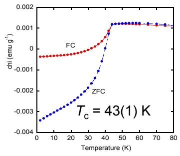
- Se-Fe-Se bond angles:

$Fe_{1.01}Se$	103.9	112.3
Our compound	102.93(6)	112.84(3)

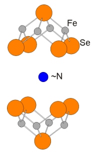
- Fe-Se bond length (Å)

$Fe_{1.01}Se$	2.3958
Our compound	2.438(1) [consistent with electron-doping]

- Li/NH_3 and Li/ND_3 produced different NPD patterns, implying that H/D is incorporated.
- No structural distortion down to 8 K



Lab powder X-ray
I4/mmm



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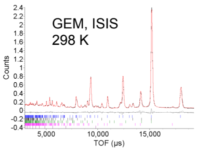
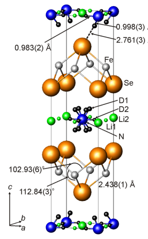
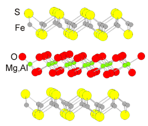
M. Burrard-Lucas, D. G. Free, S. J. Sedlmaier, J. D. Wright, S. J. Cassidy, Y. Hara, A. J. Corkett, T. Lancaster, P. J. Baker, S. J. Blundell and S. J. Clarke, Nature Materials **12**, 15 (2013)

Refined crystal structure







tochilinite
$FeS(Mg(OH)_2)_y$

Refined compositions:
$Li_{0.6(1)}ND_{2.8(1)}Fe_2Se_2$
i.e. $Li_{0.6(1)}(ND_2)_{0.2(1)}(ND_3)_{0.8(1)}Fe_2Se_2$

The Li/amide ratio implies 0.2 e^- donated per FeSe unit, consistent with $Rb_{0.3}Fe_2Se_2$ superconducting phase

M. Burrard-Lucas, D. G. Free, S. J. Sedlmaier, J. D. Wright, S. J. Cassidy, Y. Hara, A. J. Corkett, T. Lancaster, P. J. Baker, S. J. Blundell and S. J. Clarke, Nature Materials **12**, 15 (2013)

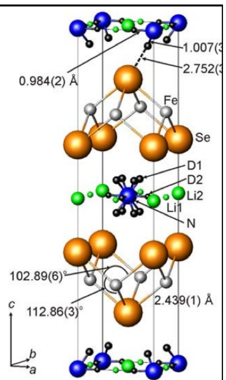
Molecular intercalation of FeSe

$FeSe_{1-\delta}$ T_c=10(2) K

Intercalation of a molecular spacer layer

$Li_x(NH_2)_y(NH_3)_{1-y}Fe_2Se_2$
(x ~0.6 ; *y* ~ 0.2)

T_c=43(1) K



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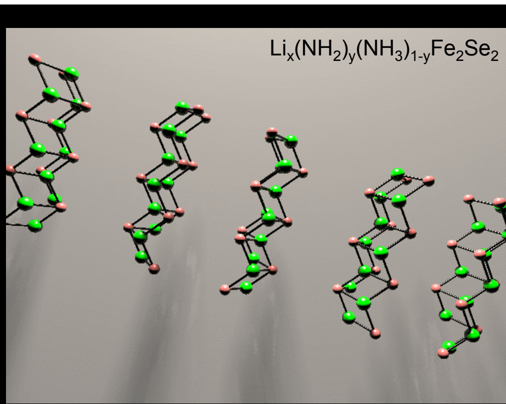


Muon spin rotation (μSR)

- Muons produced via pion decay:

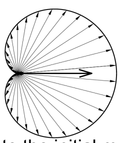
$$\pi^+ \to \mu^+ + \nu_\mu$$

PION MUON NEUTRINO

- Muons 100% spin polarized, speed~*c*/4, K.E.~4 MeV.
- Muon decays into a positron:

$$\mu^+ \to e^+ + \nu_e + \bar{\nu}_\mu$$

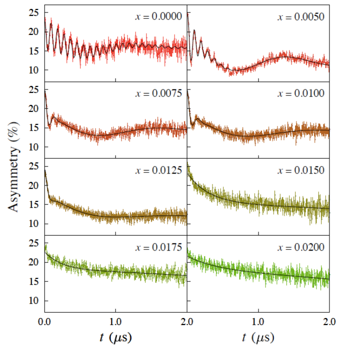
MUON POSITRON NEUTRINOS



- Positron decay is asymmetric with respect to the initial muon-spin polarization because of parity violation (weak interaction)

(see S.J. Blundell, Contemp. Phys. **40**, 175 (1999))

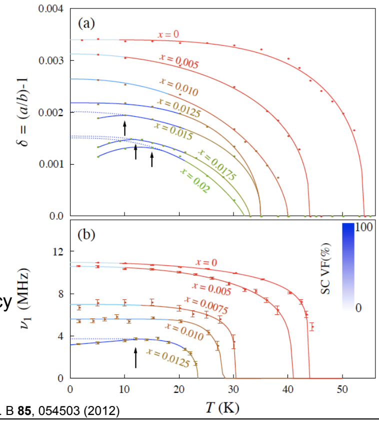
$NaFe_{1-x}Co_xAs$



D. R. Parker et al. Phys. Rev. Lett. **104**, 057007 (2010)
J. D. Wright et al. Phys. Rev. B **85**, 054503 (2012)

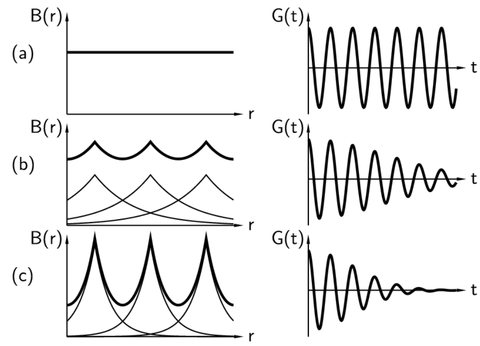
structural distortion

precession frequency



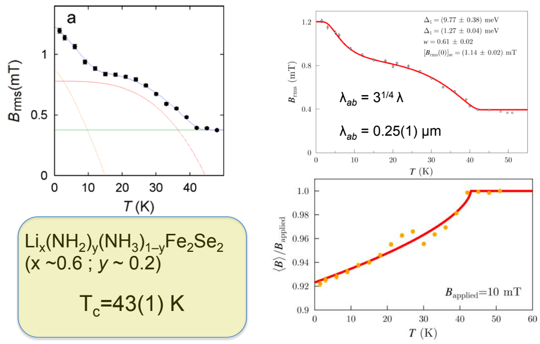
J. D. Wright et al. Phys. Rev. B **85**, 054503 (2012)

Muons and penetration depth



S.J. Blundell, Contemp. Phys. **40**, 175 (1999))

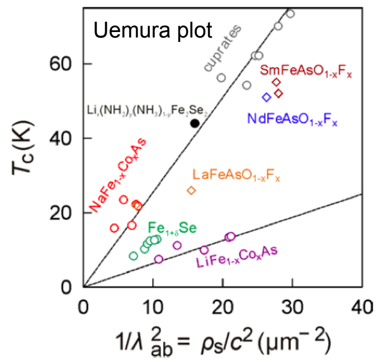
Molecular intercalation of FeSe



$Li_x(NH_2)_y(NH_3)_{1-y}Fe_2Se_2$
($x \sim 0.6$; $y \sim 0.2$)

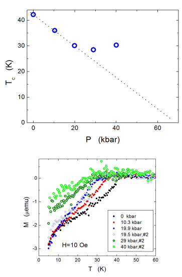
T_c=43(1) K

M. Burrard-Lucas, D. G. Free, S. J. Sedlmaier, J. D. Wright, S. J. Cassidy, Y. Hara, A. J. Corkett, T. Lancaster, P. J. Baker, S. J. Blundell and S. J. Clarke, Nature Materials **12**, 15 (2013)



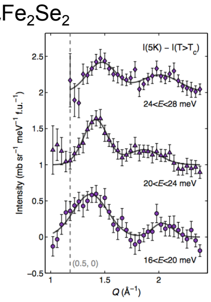
M. Burrard-Lucas, D. G. Free, S. J. Sedlmaier, J. D. Wright, S. J. Cassidy, Y. Hara, A. J. Corkett, T. Lancaster, P. J. Baker, S. J. Blundell and S. J. Clarke, Nature Materials **12**, 15 (2013)
J. D. Wright et al. Phys. Rev. B **85**, 054503 (2012)

$Li_x(NH_2)_y(NH_3)_{1-y}Fe_2Se_2$



T_c goes down with pressure
(you don't need pressure to select one nematic domain)

A. Maisuradze, R. Khasanov



Evidence for neutron resonance

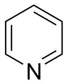
A.E. Taylor et al.,
Phys. Rev. B 87, 220508(R) (2013)

Outline

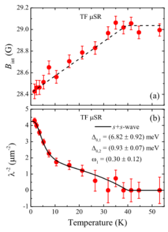
① **Introduction**
② **Intercalation** – adding new layers
③ Molecular intercalated iron-based superconductor: $\mathbf{Li_x(NH_2)_y(NH_3)_{1-y}Fe_2Se_2}$
④ Other molecular intercalated iron-based superconductors
⑤ $\mathbf{Li_{1-x}Fe_x(OH)Fe_{1-y}Se}$ – a continuously tunable superconductor

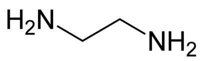
$Li_x(C_5H_5N)_yFe_2Se_2$ $Li_x(C_2H_8N_2)_yFe_{2-z}Se_2$

T_c =40-45 K T_c =45 K



pyridine



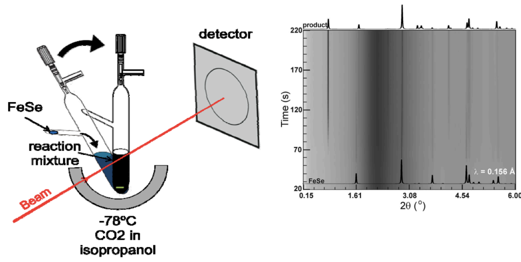


ethyldiamine

A. Krzton-Maziopa, JPCM 24, 382202 (2012)
P. K. Biswas et al. PRL 110, 137003 (2013)

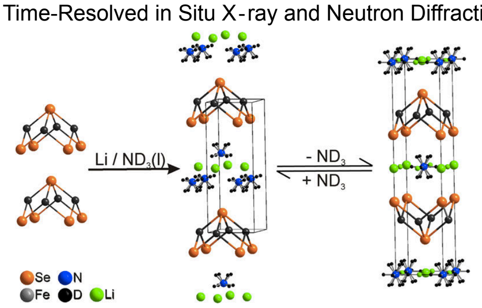
T. Hatakeda et al., JPSJ 82, 123705 (2013)

Time-Resolved in Situ X-ray and Neutron Diffraction



S. J. Sedlmaier et al., J. Am. Chem. Soc. **136**, 630 (2014)

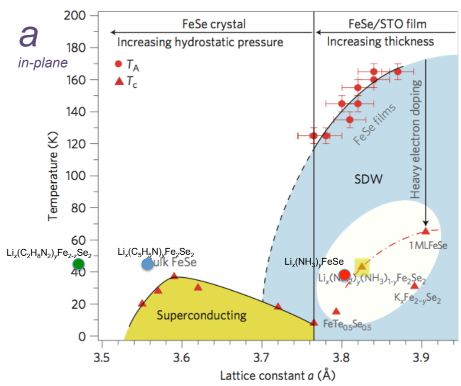
Time-Resolved in Situ X-ray and Neutron Diffraction



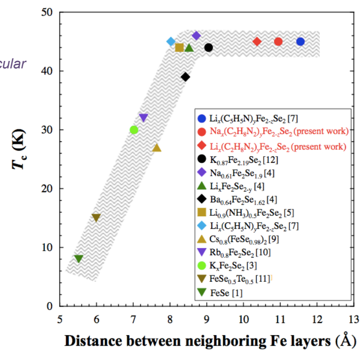
FeSe $Li_{0.6}(NH_2/NH_3)_2Fe_2Se_2$ $Li_{0.6}(NH_2/NH_3)Fe_2Se_2$

T_c=9 K T_c=39 K T_c=43 K

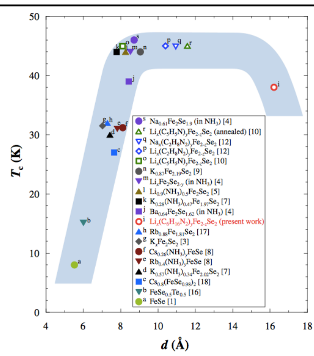
S. J. Sedlmaier et al., J. Am. Chem. Soc. **136**, 630 (2014)



S. Tan et al., Nature Materials **12**, 634 (2013)

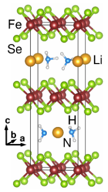


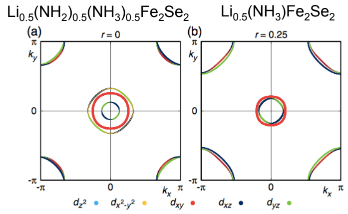
T. Noji et al., Physica C **504**, 8 (2014)



$Li_x(C_6H_{16}N_2)_yFe_{2-z}Se_2$

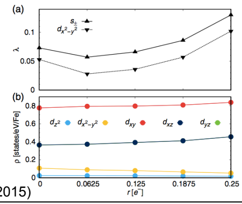
S. Hosono et al., J. Phys. Soc. Jpn. **83**, 113704 (2014)





Experimental compound: $Li_{0.6}(NH_2)_{0.2}(NH_3)_{0.8}Fe_2Se_2$

These calculations show that the electron-phonon coupling constant increases with doping, as does the density of states at E_F, but note that the compositions don't match the experimental ones (because of supercell limitations).



D. Guterding et al., Phys. Rev. B **91**, 041112(R) (2015)

Outline

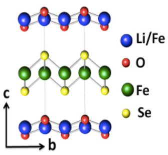
① **Intercalation** – adding new layers

② Molecular intercalated iron-based superconductor: $\mathbf{Li_x(NH_2)_y(NH_3)_{1-y}Fe_2Se_2}$

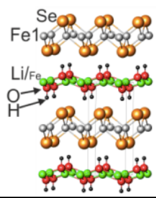
③ Other molecular intercalated iron-based superconductors

④ $\mathbf{Li_{1-x}Fe_x(OH)Fe_{1-y}Se}$ – a continuously tunable superconductor

$Li_{1-x}Fe_x(OH)Fe_{1-y}Se$



$LiFeO_2Fe_2Se_2$ reported by
X. F. Lu et al. Phys. Rev. B **89**, 020507(R) (2013)

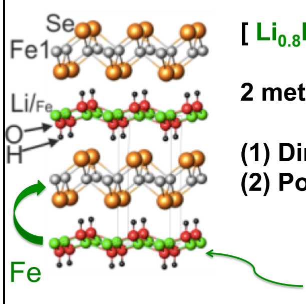


Structure wrong, and corrected by:

- H. Sun et al., Inorg. Chem. **54**, 1958 (2015)
- U. Pachmayr et al., Angew. Chem. Int. Ed. **54**, 293 (2015)
- X. F. Lu et al. Nat. Mat. **14**, 325 (2015)

$\mathbf{Li_{1-x}Fe_x(OH)Fe_{1-y}Se}$

$Li_{1-x}Fe_x(OH)Fe_{1-y}Se$



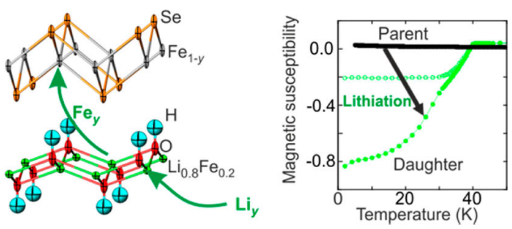
[$Li_{0.8}Fe_{0.2}(OH)$] [$Fe_{1-y}Se$]

2 methods of control:

(1) Directly control of *y*
(2) Post synthetic lithiation

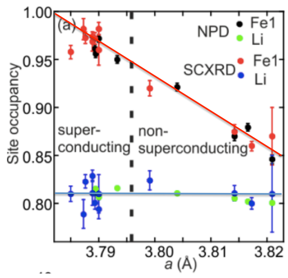
H. Sun, et al. Inorg. Chem. **54**, 1958 (2015)

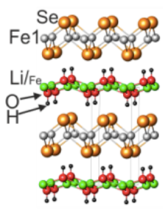
$Li_{1-x}Fe_x(OH)Fe_{1-y}Se$



H. Sun, et al. Inorg. Chem. **54**, 1958 (2015)

$Li_{1-x}Fe_x(OH)Fe_{1-y}Se$

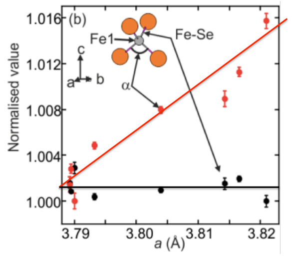


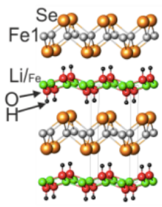


The only significant structural change is the Fe1 occupancy (in the FeSe layers), correlated with a reduction in the *a* lattice parameter

H. Sun, et al. Inorg. Chem. **54**, 1958 (2015)

$Li_{1-x}Fe_x(OH)Fe_{1-y}Se$

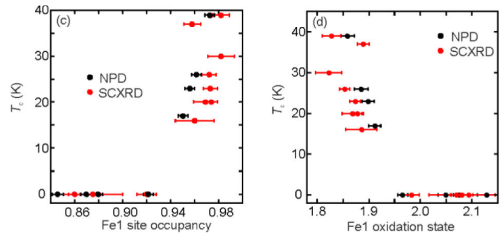




The Fe-Se distance is invariant across the series
The Se-Fe-Se angle changes

H. Sun, et al. Inorg. Chem. **54**, 1958 (2015)

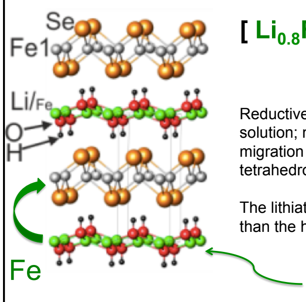
$Li_{1-x}Fe_x(OH)Fe_{1-y}Se$



The Fe1 occupancy then controls T_c, and is correlated with the Fe1 oxidation state

H. Sun, et al. Inorg. Chem. **54**, 1958 (2015)

$Li_{1-x}Fe_x(OH)Fe_{1-y}Se$



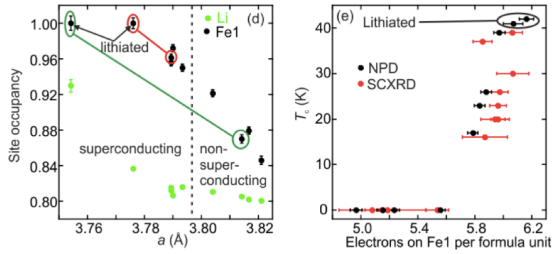
[$Li_{0.8}Fe_{0.2}(OH)$] [$Fe_{1-y}Se$]

Reductive litiation step using lithium/NH3 solution; metal hydroxide layer relatively flat; migration occurs via the face of a Se4 tetrahedron.

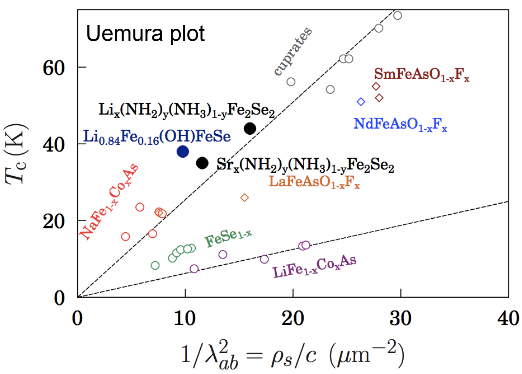
The lithiated samples are more air-sensitive than the hydrothermally synthesized parents

H. Sun, et al. Inorg. Chem. **54**, 1958 (2015)

$Li_{1-x}Fe_x(OH)Fe_{1-y}Se$



H. Sun, et al. Inorg. Chem. **54**, 1958 (2015)



M. Burrard-Lucas et al. Nature Materials **12**, 15 (2013)
H. Sun, et al. Inorg. Chem. **54**, 1958 (2015)
F. R. Foronda et al., in preparation.

Summary

Molecules to build superconductors?

Molecular superconductors are already well studied, but there is now a novel way to make them!

Low-temperature intercalation is a powerful new method that holds a lot of promise in iron pnictides. Hydrothermal synthesis, and post-synthetic treatments, provide materials with continuously tunability of T_c and in which the tetragonal phase is stabilised by the inserted interlayers (the insertion brings the system into "natural harmony").

These may be effective new strategies to navigate the maze.