

# Doping dependence of superconducting transition temperatures in alkali metal/ammonia intercalated FeSe

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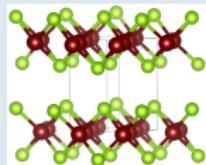
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# Superconductivity of iron selenide and derived materials

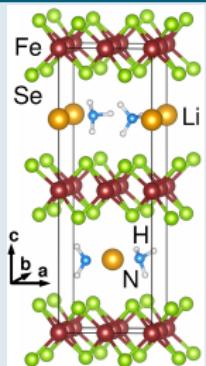
## FeSe

- bulk superconductor with  $T_c = 8 \text{ K}$
- $T_c \sim 40 \text{ K}$  under pressure of  $\sim 10 \text{ GPa}$
- structurally the most simple Fe-based SC, but physics is poorly understood



## intercalated FeSe

- hard to synthesize bulk materials
- e.g.  $K_xFe_{2-y}Se_2$  only gives SC grains with  $T_c \sim 30 \text{ K}$
- new synthesis method with organic solvents gives  $T_c \sim 46 \text{ K}$
- e.g.  $Li_x(NH_2)_y(NH_3)_zFe_2Se_2$  with  $T_c \sim 44 \text{ K}$



# Material dependence of $T_c$ in intercalated FeSe

- many alkali metal/solvent combinations possible
- linear dependence of  $T_c$  on FeSe layer separation from 5 to 9 Å**
- constant  $T_c$  beyond 9 Å
- most of the materials have different nominal doping level
- no simple connection between charge doping and  $T_c$
- more doped materials like  $\text{Rb}_{0.8}\text{Fe}_2\text{Se}_2$  have lower  $T_c$  than less doped materials like  $\text{Na}_{0.61}\text{Fe}_2\text{Se}_{1.9}$**

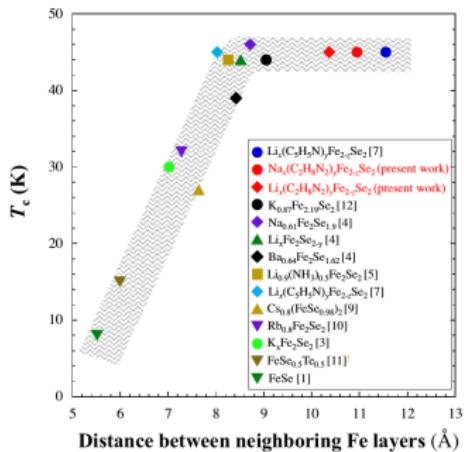


Figure : Noji et al., Physica C **504**, 8 (2014)

# Crystal structure and properties of lithium/ammonia intercalated FeSe

- lithium atoms are dissolved in liquid ammonia ( $\text{NH}_3$ )
- ammonia rich and ammonia poor crystals can be synthesized
- $\text{Li}_{0.56}(\text{NH}_2)_{0.53}(\text{NH}_3)_{1.19}\text{Fe}_2\text{Se}_2$  has  $T_c = 39 \text{ K}$  and  $c = 10.3 \text{ \AA}$
- $\text{Li}_{0.6}(\text{NH}_2)_{0.2}(\text{NH}_3)_{0.8}\text{Fe}_2\text{Se}_2$  has  $T_c = 44 \text{ K}$  and  $c = 8.1 \text{ \AA}$
- **larger c-axis gives lower  $T_c$**
- $[\text{NH}_2]^-$  is a radical, should oxidize Li
- charge doping is important!

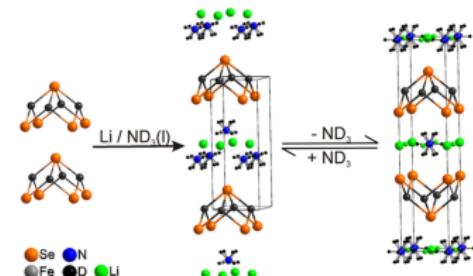
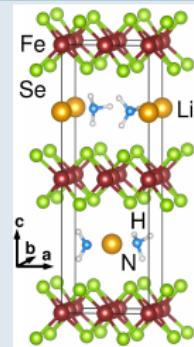


Figure : Sedlmaier et al., J. Am. Chem. Soc. **136**, 630 (2014)

# *Ab-initio* calculations for lithium/ammonia intercalated FeSe

## Idealized structure

- lattice parameters and FeSe layer from exp.
- construct super cell with Li:Fe ratio close to exp.
- remove fractional occupations of Li, N and H
- relax all hydrogen positions (GPAW DFT code)
- result:  $\text{Li}_{0.5}(\text{NH}_3)\text{Fe}_2\text{Se}_2$  and  $\text{Li}_{0.5}(\text{NH}_3)_2\text{Fe}_2\text{Se}_2$



## Electronic band structure analysis

- full potential local orbital (FPLO) code
- band structure unfolding (Tomić et al., PRB (in press))
- projective Wannier functions (16-, 10-, 8- and 5-band models)
- simulate  $\text{NH}_2$  with virtual crystal approximation (VCA)

# Simulation of NH<sub>2</sub> content within VCA

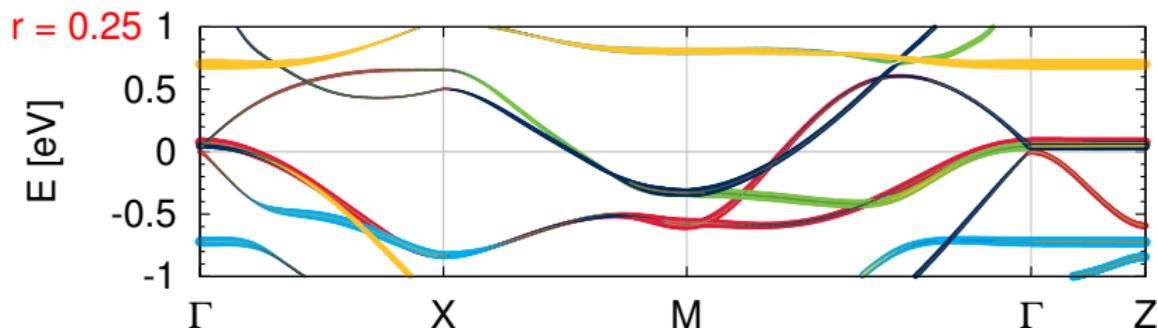
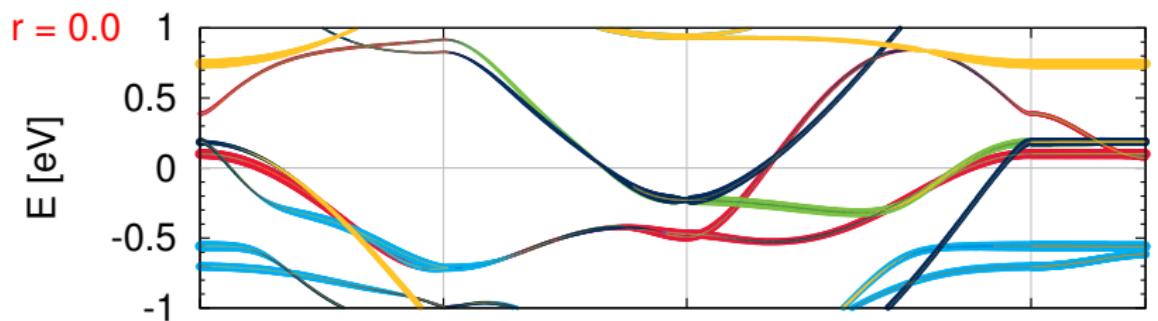
- VCA interpolates continuously between atom with nuclear charge  $Z$  and atom with nuclear charge  $Z - 1$  or  $Z + 1$
- fractionally replacing N ( $Z = 7$ ) by C ( $Z = 6$ ) **interpolates between neutral NH<sub>3</sub> and CH<sub>3</sub> radical**
- use notation  
 $\text{Li}_{0.5}(\text{NH}_2)_{0.5-2r}(\text{NH}_3)_{0.5+2r}\text{Fe}_2\text{Se}_2$
- $r = \{0.0, \dots, 0.25\}$  is the **number of nominally doped e<sup>-</sup>/Fe**
- VCA agrees well with explicit removal of H atoms
- H bands at Fermi level then prevent good fit of band structure



$r=0.25$

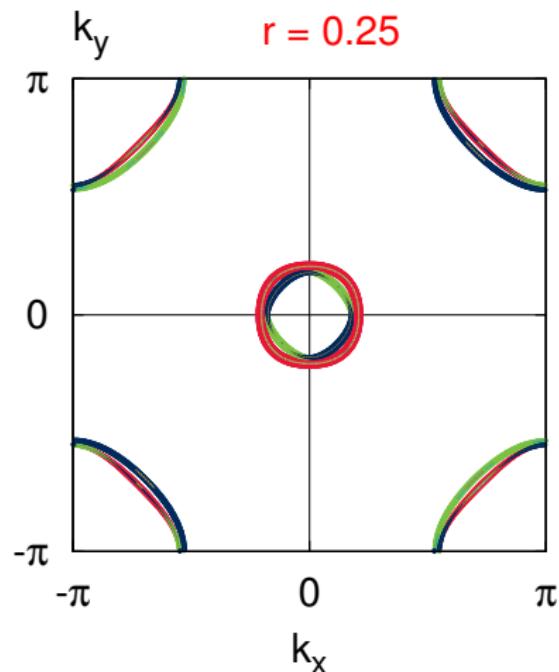
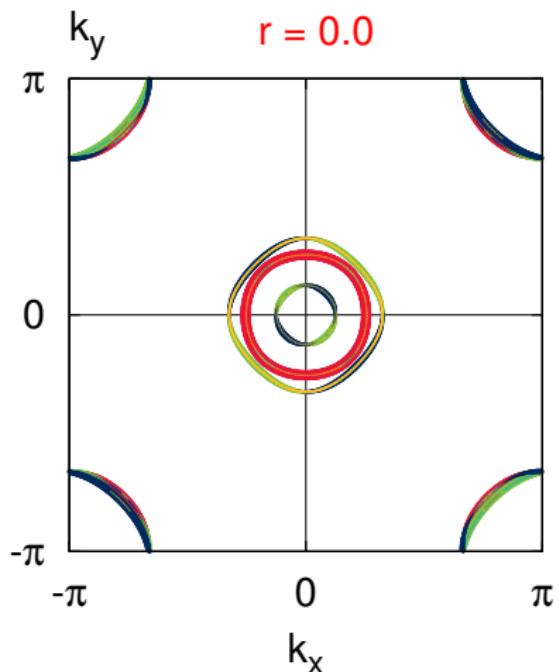
$r=-0.25$

# Band structure within the 16-band model



$d_z^2$  ●  $d_{x^2-y^2}$  ●  $d_{xy}$  ●  $d_{xz}$  ●  $d_{yz}$  ●

# Fermi surface within the 16-band model



$d_z^2$    ●    $d_{x^2-y^2}$    ●    $d_{xy}$    ●    $d_{xz}$    ●    $d_{yz}$    ●

# Summary of band structure and Fermi surface analysis

## Importance of NH<sub>2</sub>

- $r = 0$  gives electronic structure like undoped material
- NH<sub>2</sub> content indeed controls the doping level



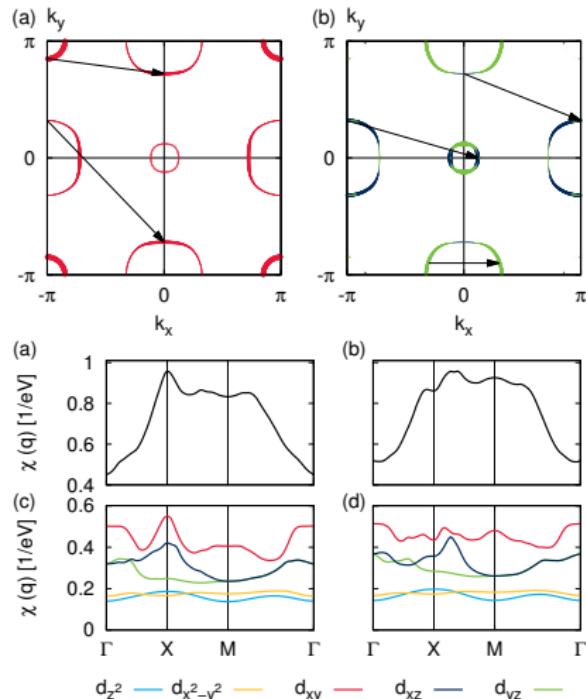
- $T_c = 39$  K and  $c = 10.3$  Å
- $r = 0.015$ , almost no electron doping



- has  $T_c = 44$  K and  $c = 8.1$  Å
- $r = 0.2$ , strongly electron doped

# Non-interacting susceptibility in the 8-band model

- non-interacting susceptibility reveals magnetic instabilities
- electron doping destroys  $(\pi, 0)$  nesting
- no stripe AFM** is to be expected for electron doped intercalates
- agrees with neutron scattering exp.** (Taylor et al., PRB **87**, 220508 (2014))

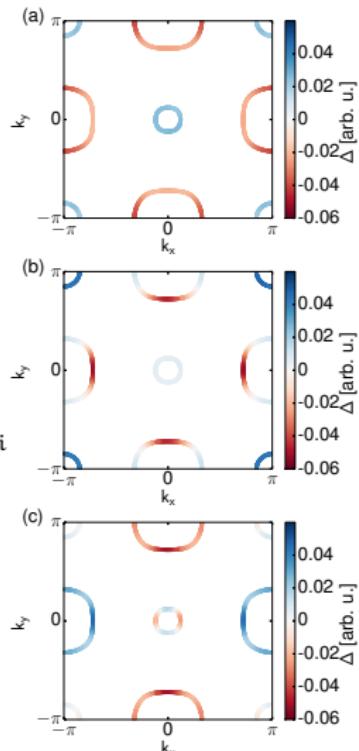
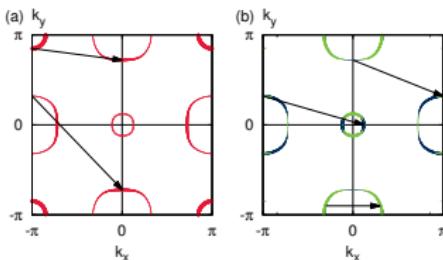


$$\chi_{st}^{pq}(\vec{q}) = -\frac{1}{N} \sum_{\vec{k}, \mu, \nu} a_\mu^s(\vec{k}) a_\mu^{p*}(\vec{k}) a_\nu^q(\vec{k} + \vec{q}) a_\nu^{t*}(\vec{k} + \vec{q}) \frac{f(E_\nu(\vec{k} + \vec{q})) - f(E_\mu(\vec{k}))}{E_\nu(\vec{k} + \vec{q}) - E_\mu(\vec{k})}$$

# RPA spin-fluctuation pairing in the 8-band model

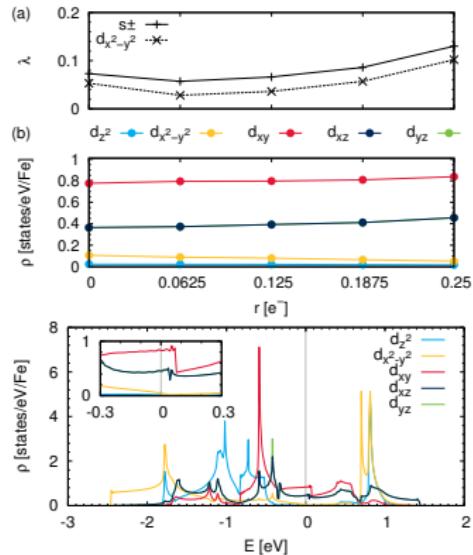
- spin-fluctuations can bind cooper pairs
- calculate pairing interaction within random phase approximation (RPA)  
(Graser et al., New J. Phys. **11**, 025016 (2009))
- leading  $s\pm$  instability, subleading  $d_{x^2-y^2}$

$$-\sum_j \oint_{C_j} \frac{d\vec{k}_\parallel}{2\pi} \frac{1}{4\pi v_F(\vec{k}') } \left[ \Gamma_{ij}(\vec{k}, \vec{k}') + \Gamma_{ij}(\vec{k}, -\vec{k}') \right] g_j(\vec{k}') = \lambda_i g_i$$



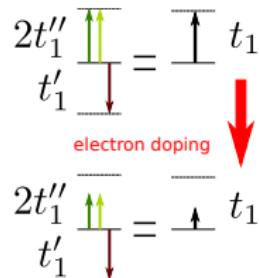
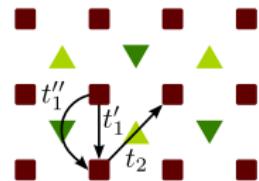
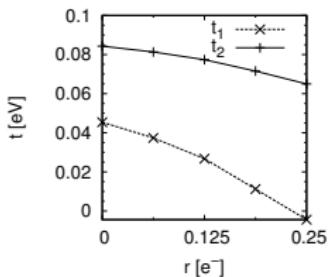
# Doping dependence of the SC pairing strength

- constant interaction parameters  
 $U = 1.35 \text{ eV}$ ,  $U' = U/2$ ,  
 $J = J' = U/4$
- pairing strength  $\lambda$  drops initially as nesting is destroyed, then increases with electron doping
- hole pockets are on the verge of disappearing
- electron doping increases DOS at the Fermi level
- leads to enhanced spin-fluctuations, i.e. stronger pairing
- e.g.  $K_xFe_{2-y}Se_2$  has lower  $T_c$  because hole pockets are gone



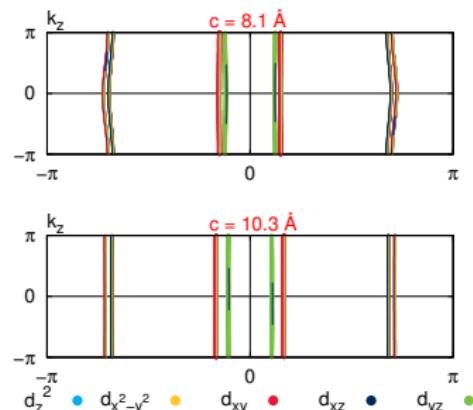
# Microscopic origin of the DOS enhancement

- shift of the bands is not rigid
- next-neighbor hopping in  $d_{xy}$  orbital is strongly reduced
- direct and indirect contributions to  $t_1$  have different sign
- indirect process dominates at low doping
- states from Se are lowered in energy due to positive charge in the interlayer
- indirect hopping decreases, cancellation at maximum doping
- bandwidth reduction and Fermi level shift work together to enhance the pairing
- lower two figures adapted from Suzuki et al., PRL **113**, 027002 (2014)



# Relative importance of c-axis height and electron doping

- doping dependence was extracted based on ammonia poor compound
- ammonia poor compound has slight corrugation on the Fermi surface cylinders
- higher c-axis makes ammonia rich perfectly 2D
- ammonia rich compound has higher  $\lambda$  at **identical doping level**
- in reality it has lower  $T_c$
- **actual charge doping level makes the difference** in the 2D limit
- FS becomes 2D with c-axis of  $\sim 9 \text{ \AA}$



# Summary

- 2D Fermi surface favors high  $T_c$
- in 2D limit electron doping enhances  $T_c$
- dimensionality and electron doping can be controlled through the interlayer chemistry
- increase of c-axis beyond 9 Å does not increase  $T_c$  **because system is already 2D**
- intercalates without hole pockets have low  $T_c$  because large DOS is somewhere below Fermi level
- preprint: [arXiv:1410.7565](https://arxiv.org/abs/1410.7565)

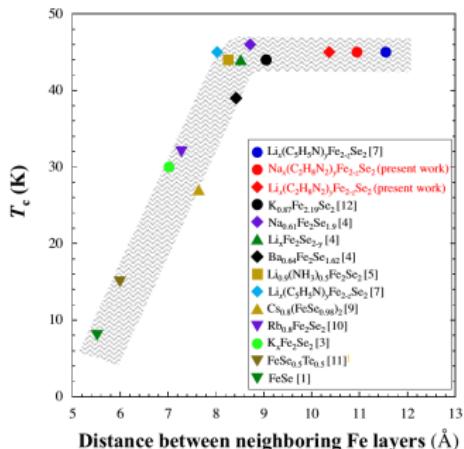


Figure : Noji et al., Physica C 504, 8 (2014)