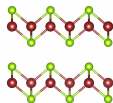


Doping dependence of superconducting transition temperatures in alkali metal/ammonia intercalated FeSe

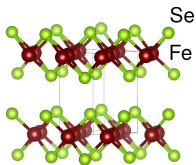
Daniel Guterding, Harald O. Jeschke, Peter J. Hirschfeld, and Roser Valentí
Institut für Theoretische Physik

March 4, 2015



Superconductivity of iron selenide and derived materials

- synthesis of intercalates possible with many alkali metal/solvent combinations



- linear dependence of T_c on FeSe layer separation from 5 to 9 Å
- constant T_c beyond 9 Å
- different nominal doping levels

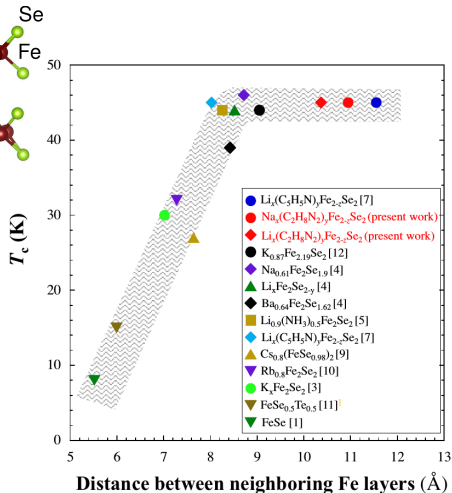
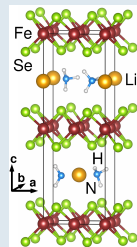


Figure : Noji et al., Physica C **504**, 8 (2014)

Ab-initio calculations for lithium/ammonia intercalated FeSe

Idealized structure

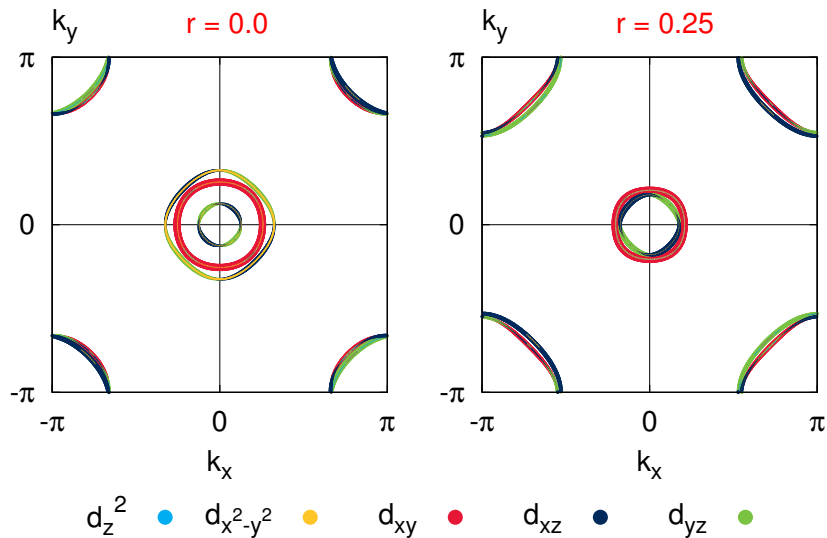
- $\text{Li}_x(\text{NH}_2)_y(\text{NH}_3)_z\text{Fe}_2\text{Se}_2$ with $T_c \sim 44$ K
- lattice parameters and FeSe layer from exp.
Burrard-Lucas et al., Nat. Mater. **12**, 15 (2013)
Sedlmaier et al., JACS **136**, 630 (2014)
- construct super cell with Li:Fe ratio close to exp.
- result: $\text{Li}_{0.5}(\text{NH}_3)\text{Fe}_2\text{Se}_2$, $0.25 e^-$ per Fe doping



Electronic band structure analysis

- full potential local orbital (FPLO) code
- band structure unfolding (*Tomić, Jeschke, Valentí, PRB 90, 195121 (2014)*)
- projective Wannier functions (16-, 10-, 8- and 5-band models)
- simulate NH_2 with virtual crystal approximation (VCA)

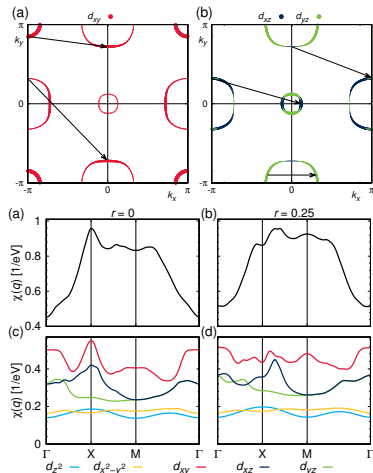
Fermi surface within the 16-band model



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

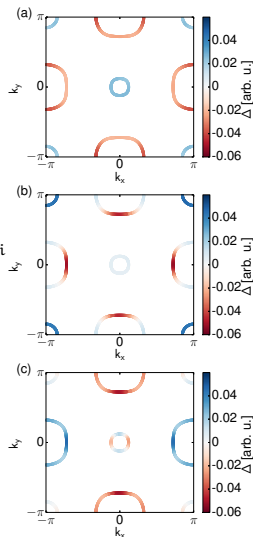
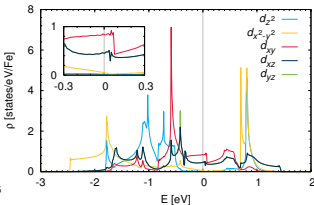
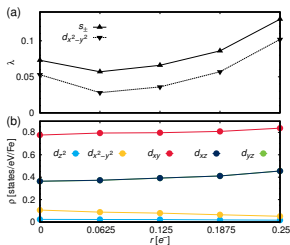
- calculate pairing interaction within random phase approximation (RPA)

Bickers, Scalapino, White, PRL **62**, 961 (1989)

Graser, Maier, Hirschfeld, Scalapino, New J. Phys. **11**, 025016 (2009)

- leading s_{\pm} instability, subleading $d_{x^2-y^2}$

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



Summary

- 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
- published: **Guterding et al., PRB 91, 041112(R) (2015)**

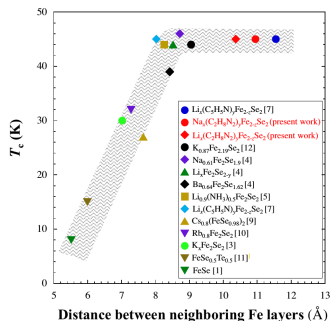


Figure : Noji et al., Physica C 504, 8 (2014)

Crystal structure and properties of lithium/ammonia intercalated FeSe

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

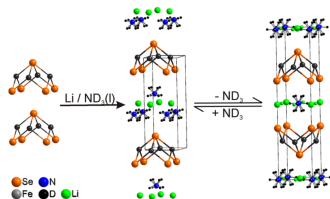
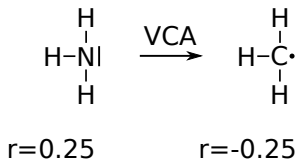


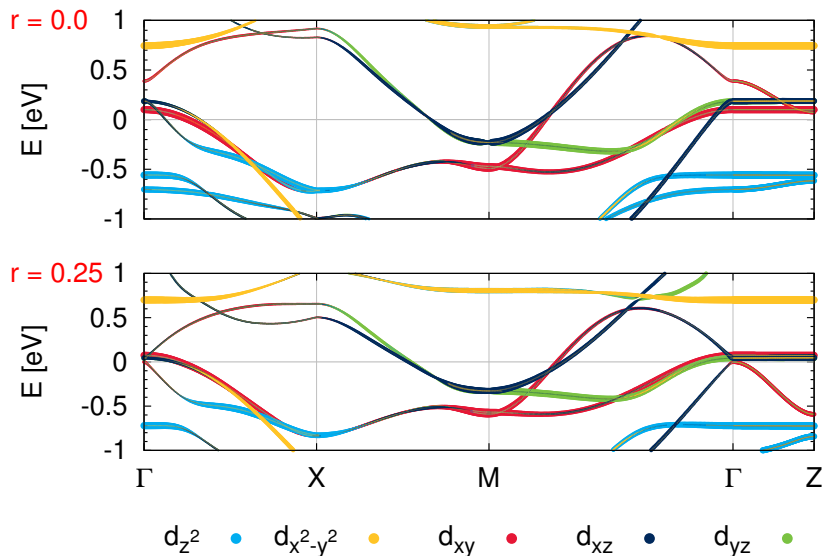
Figure : Sedlmaier et al., J. Am. Chem. Soc. **136**, 630 (2014)

Simulation of NH_2 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_3 and CH_3 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^-/Fe**
- VCA agrees well with explicit removal of H atoms
- H bands at Fermi level then prevent good fit of band structure



Band structure within the 16-band model



Summary of band structure and Fermi surface analysis

Importance of NH_2

- $r = 0$ gives electronic structure like undoped material
- NH_2 content indeed controls the doping level

$\text{Li}_{0.56}(\text{NH}_2)_{0.53}(\text{NH}_3)_{1.19}\text{Fe}_2\text{Se}_2$ (exp. ammonia rich)

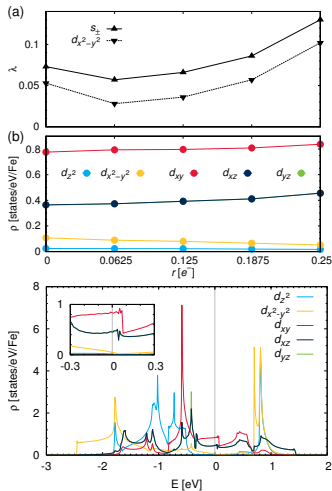
- $T_c = 39$ K and $c = 10.3$ Å
- $r = 0.015$, almost no electron doping

$\text{Li}_{0.6}(\text{NH}_2)_{0.2}(\text{NH}_3)_{0.8}\text{Fe}_2\text{Se}_2$ (exp. ammonia poor)

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

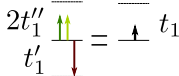
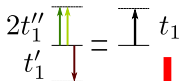
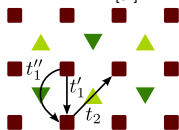
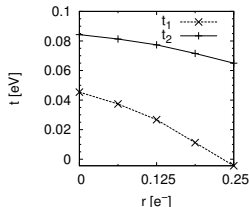
Doping dependence of the SC pairing strength

- constant interaction parameters
 $U = 1.35$ eV, $U' = U/2$,
 $J = J' = U/4$
- pairing strength λ 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. $K_x\text{Fe}_{2-y}\text{Se}_2$ has lower T_c because hole pockets are gone



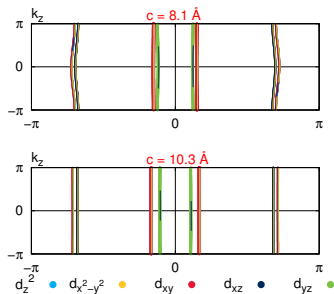
Microscopic origin of the DOS enhancement

- 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 λ 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 $\sim 9 \text{ \AA}$



Tight binding+RPA formalism in a nutshell

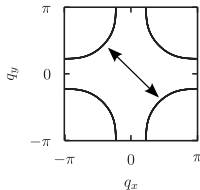
$$\chi_{st}^{pq}(\vec{q}) = -\frac{1}{N} \sum_{\vec{k}, \mu, \nu} a_{\mu}^s(\vec{k}) a_{\mu}^{p*}(\vec{k}) a_{\nu}^q(\vec{k}+\vec{q}) a_{\nu}^{t*}(\vec{k}+\vec{q}) \frac{f(E_{\nu}(\vec{k}+\vec{q})) - f(E_{\mu}(\vec{k}))}{E_{\nu}(\vec{k}+\vec{q}) - E_{\mu}(\vec{k})}$$

$$[(\chi_{\text{spin}}^{\text{RPA}})_{st}^{pq}]^{-1} = [\chi_{st}^{pq}]^{-1} - (\mathbf{U}_{\text{spin}})_{st}^{pq}$$

$$\Gamma_{st}^{pq}(\vec{k}, \vec{k}') = \left[\frac{3}{2} \mathbf{U}_s \chi_s^{\text{RPA}}(\vec{k} - \vec{k}') \mathbf{U}_s + \frac{1}{2} \mathbf{U}_s - \frac{1}{2} \mathbf{U}_c \chi_c^{\text{RPA}}(\vec{k} - \vec{k}') \mathbf{U}_c + \frac{1}{2} \mathbf{U}_c \right]_{ps}^{tq}$$

$$\Gamma_{ij}(\vec{k}, \vec{k}') = \sum_{stpq} a_i^{t*}(-\vec{k}) a_i^{s*}(\vec{k}) \text{Re} \left[\Gamma_{st}^{pq}(\vec{k}, \vec{k}') \right] a_j^p(\vec{k}') a_j^q(-\vec{k}')$$

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



- Graser, Maier, Hirschfeld, Scalapino, *New Journal of Physics* **11**, 025016 (2009)

Other interesting talks

- **Z5.00004** : Generalized unfolding method, **Friday 11:15 AM**, Milan Tomić