Hyperfine interactions in superconducting KFe_2Se_2

I. Madjarevic[a], V. Koteski[a], V. Ivanovski[a], C. Petrovic[b]

[a] Laboratory of Nuclear and Plasma Physics, University of Belgrade, Vinča Institute of Nuclear Sciences, 11001 Belgrade, Serbia

[b] Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA

Iron-based superconductors

- **$La[O_{1-x}F_x]FeAs$ –** *Kamihara et al. [2008]* [1]

  → superconductivity + magnetism !!!!

- layered structure based on a square planar Fe^{2+} layer
tetrahedrally coordinated pnictogen (P, As)
or chalcogen (S, Se, Te) anions.

- **Classes:**

1. Doped RE 1111 Fe-pnictide, T_c ~ 25–55K,
2. Doped A 122 (A = Ba,Sr)($Ba_{1-x}K_xFe_2As_2$), T_c ~ 38 K.
3. 111 systems ($Li_{1-x}FeAs$), T_c ~ 18 K,
4. (Sr, Ca, Eu)F FeAs, Tc ~ 36 K,
5. $Sr_4(Sc, V)_2O_6Fe_2(P, As)_2$, T_c ~ 17 K,
6. $FeSe_x$, $FeSe_{1-x}Te_x$ with T_c up to 14K,
7. **$A_xFe_{2-y}Se_2$ (A = Tl,K,Rb,Cs) with T_C up to 32K**.

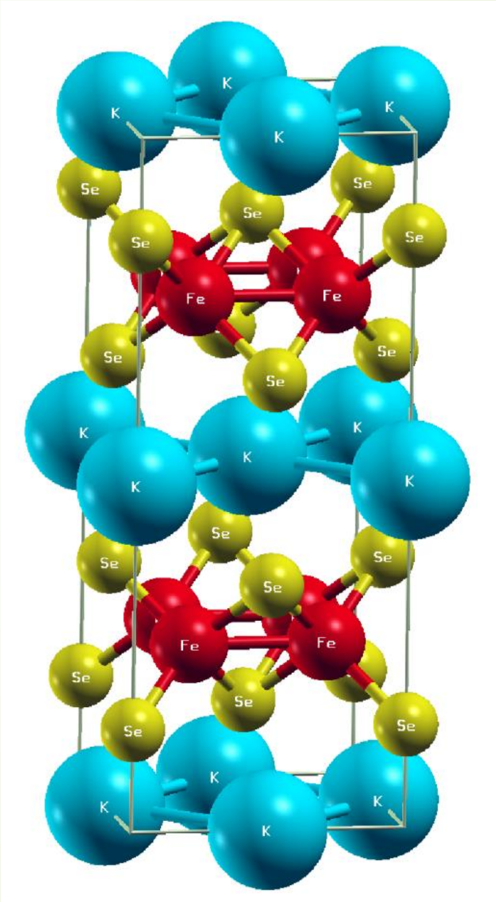
$A_xFe_{2-y}Se_2$ "enigma"

- *Guo et al. [2010]* [2] *:*
  "SC above 30 K is due to this FeSe-based 122 phase"
  - structure **I4/mmm** ($ThCr_2Si_2$ - type)
    - a = b=3.9136(1) Å,
      c=14.0367(7) Å
    - Fe in **4d** site
- normal state resistivity very large

  → **Antiferomagnetism (AFM)**
  $T_N \approx 559$ K
  large moment ~ 3.3 μ_B/Fe

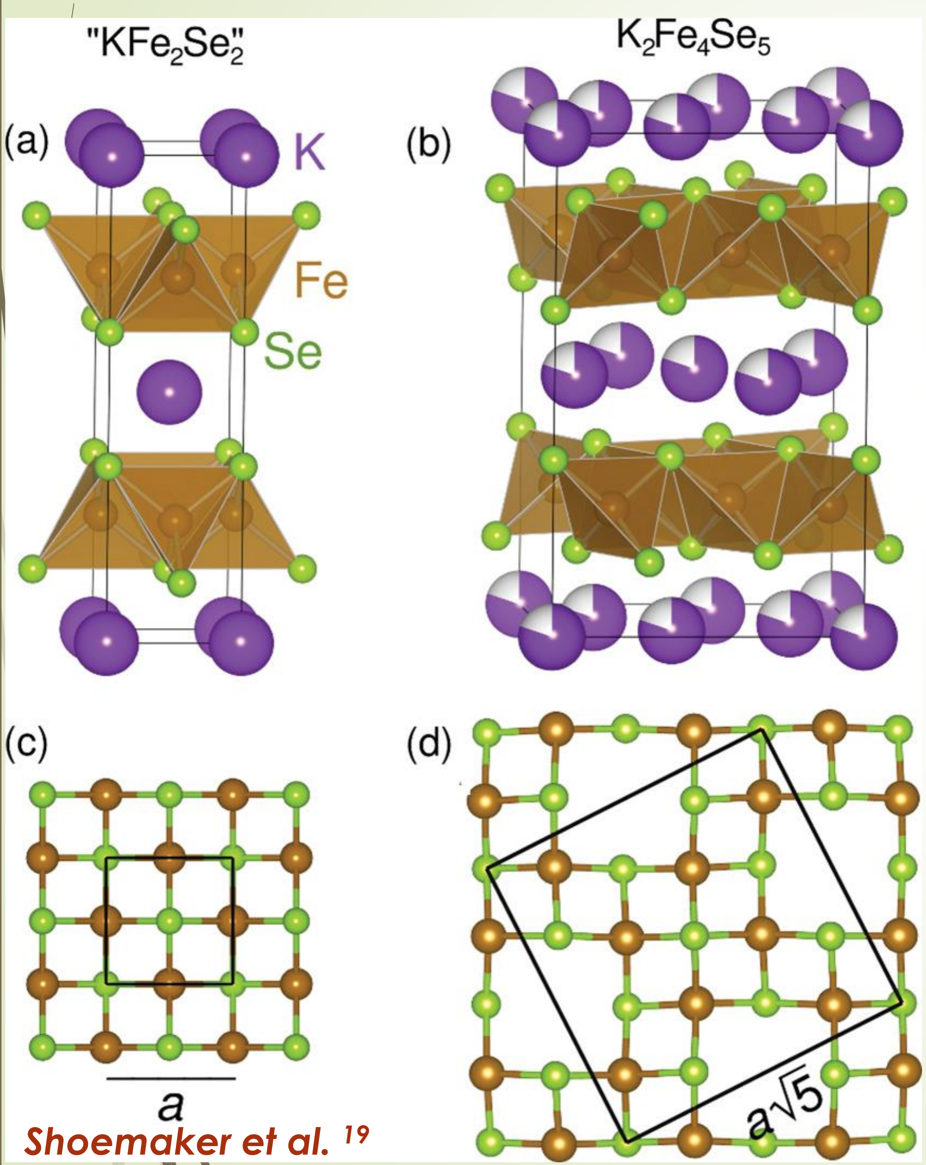
  → **Fe vacancies !!!**

- "strange" phase separation ???
- iron-based SC theory brake-down? [26-28]



made with "**XCrySDen**" software:
A. Kokalj, Comp. Mater. Sci., 2003, Vol. 28, p. 155.

$K_xFe_{2-y}Se_2$ - phase separation



Shoemaker et al. [19]

- multiple experimental evidences:
  XRD[3,4,5], Raman spect.[6]
  Neutron diff.[7,8,9,10,11,12]
  SEM[3], TEM[13,14]
  Mössbauer[15,16,17]
  EXAFS[18]

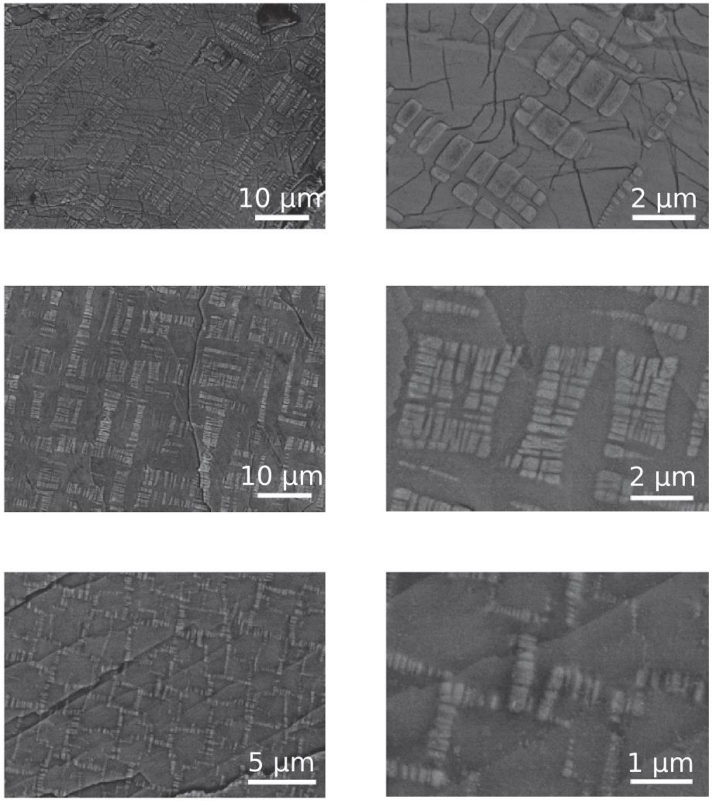
- two distinctive phases???

  - I4/mmm (122) **SC** phase (disordered Fe-vacancies)
  Fe site – *4d*
  - ***metallic***

  - I4/m (245) **AFM** phase ($\sqrt{5} \times \sqrt{5} \times 1$ Fe-vacancies structure equivalent to $K_2Fe_4Se_5$)
  Fe sites – *16i* and "empty" *4d*
  - "***Mott insulator***"

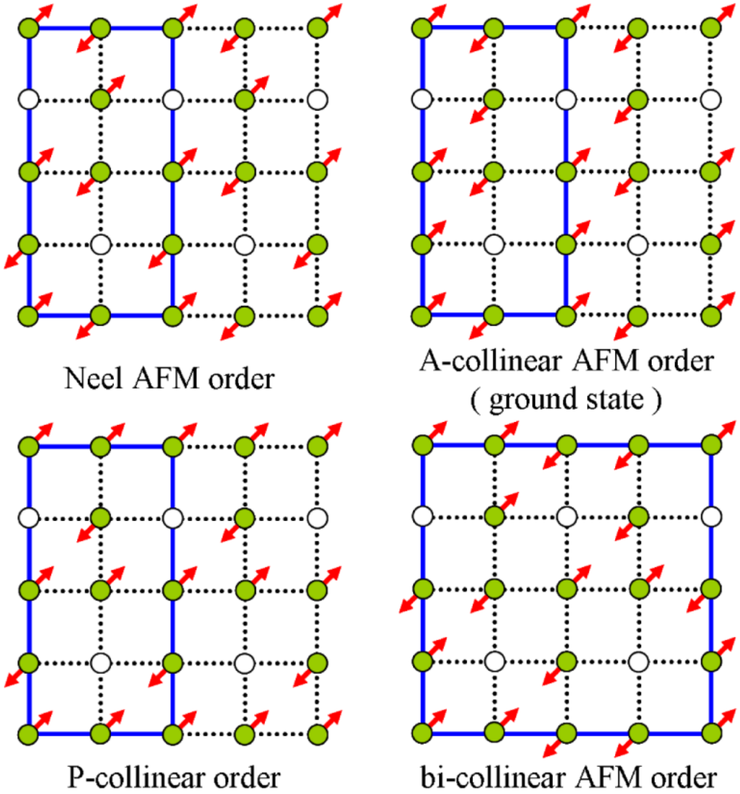
Phase separation revisited

- mesoscopic phase separation (~100 nm)
  → more phases?
  → AF parent of SC phase?



Ding et al. [3] Back-scattered electron images of SEM measurements on the cleaved surface of three typical samples

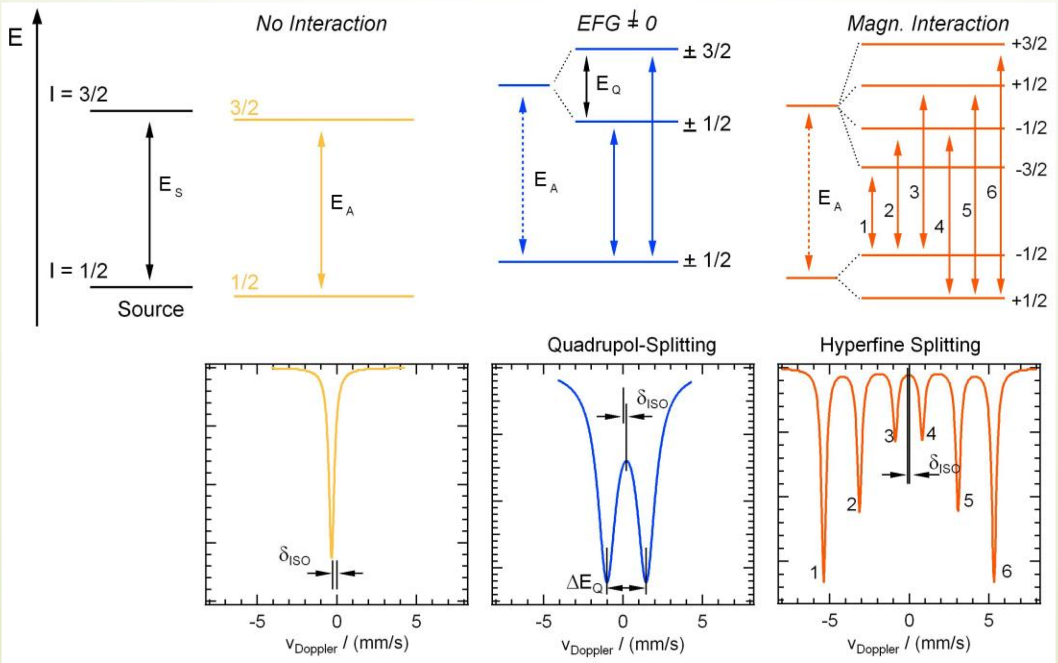
$\sqrt{2} \times \sqrt{2}$



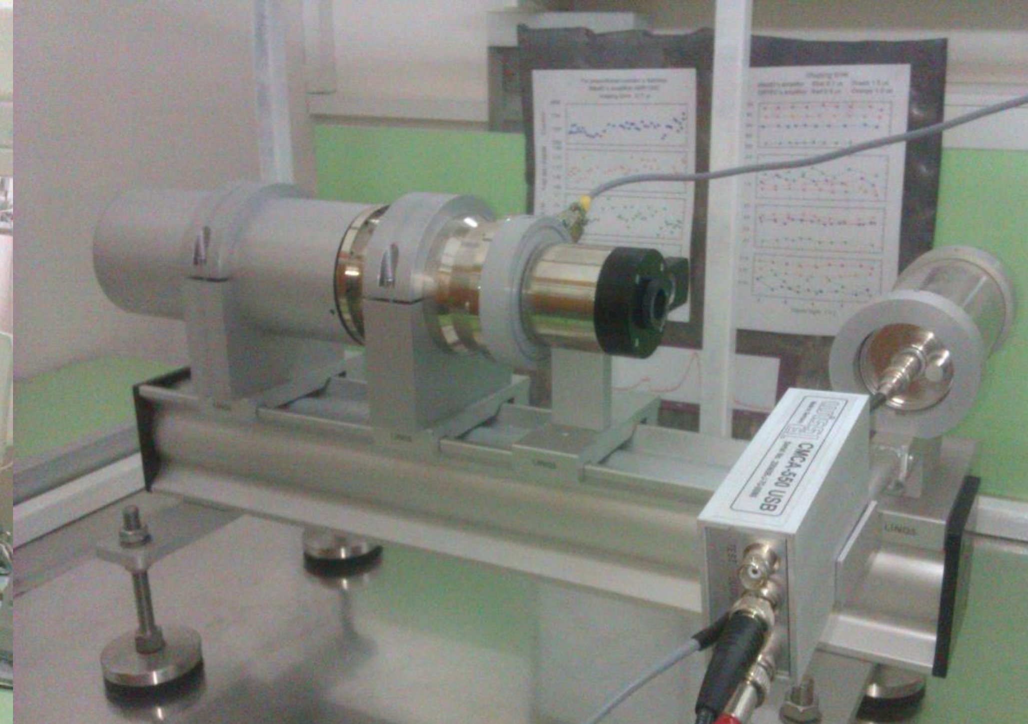
Yang et al. [20] Schematic top view of four possible magnetic orders in the Fe-Fe square layer with one quarter Fe-vacancies ordered in rhombus

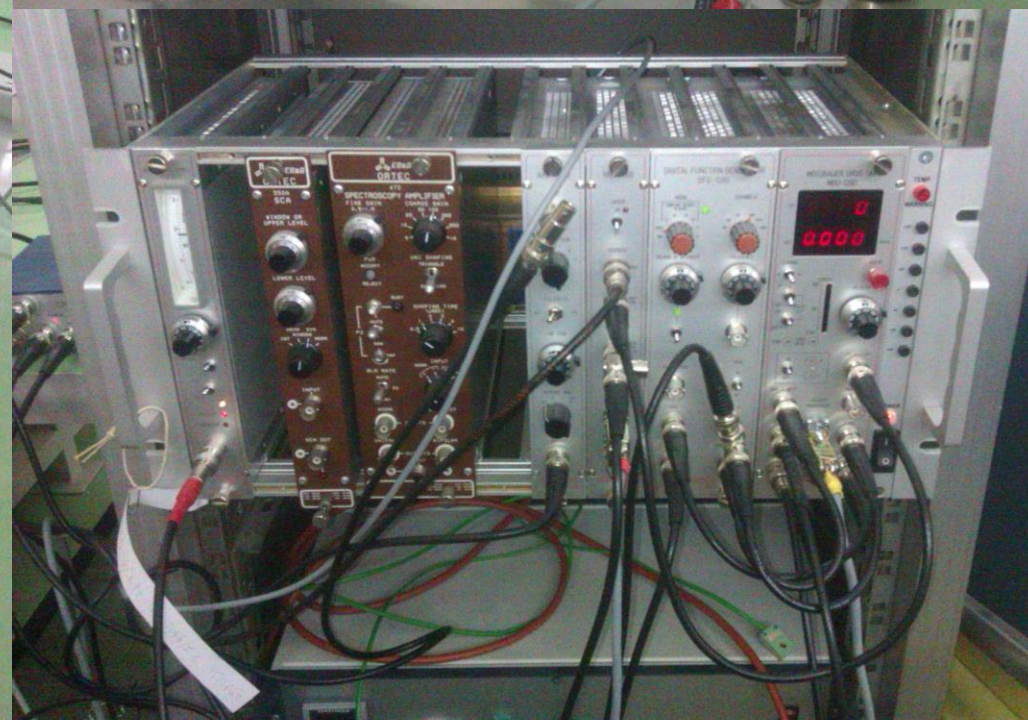
Methods:
Mössbauer spectroscopy

- nuclear method in material science
  - ^{57}Fe (E_γ = 14.4 keV) source accelerated through a range of velocities
  - 1mm/s = 48.075 neV
  - **fine speed tuning → resonant absorption on sample**
  - **absorption spectra → get hyperfine interactions information <u>relative to α-Fe</u>**
    - **- local magnetic field on Fe site**
    - **- electric field gradient - EFG**
    - **- isomer shift - IS**



Picture from:
www.helmholtz-berlin.de


CMCA-550 USB


ORTEC
SPECTROSCOPY AMPLIFIER
0.000

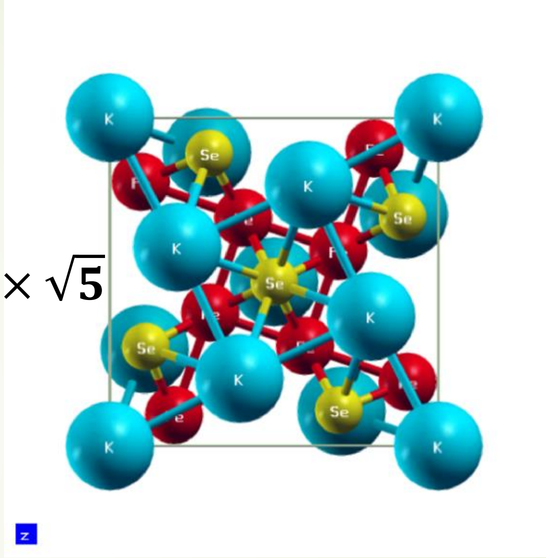
Methods: *Calculations*

- **WIEN2k**
  LAPW + local orbitals (lo) method
  GGA-PBE
  structure optimization

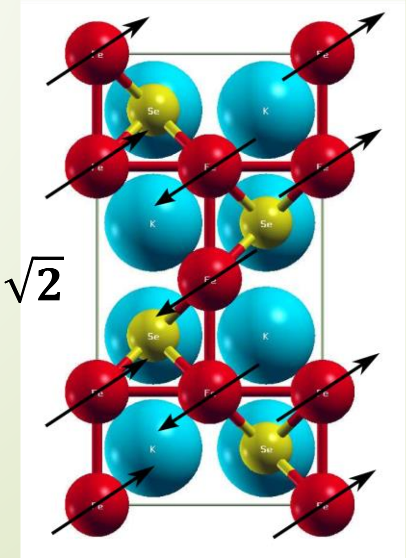
- **KFe_2Se_2**
  - I4/mmm phase without vacancies (collinear AFM)
  - I4/m phase with two vacancies orders: $\sqrt{5}\times\sqrt{5}$ and $\sqrt{2}\times\sqrt{2}$ (block AFM)

- **Comparing case $RbFe_2Se_2$**
  - I4/mmm phase without vacancies (collinear AFM)
  - I4/m phase with vacancies order: $\sqrt{5}\times\sqrt{5}$ (block AFM)
  - charged +1 I4/m phase with vacancies order: $\sqrt{5}\times\sqrt{5}$ (block AFM)

$\sqrt{5}\times\sqrt{5}$



$\sqrt{2}\times\sqrt{2}$



Sample preparation

- **KFe_2Se_2** single crystals of were grown by the *self-flux method*[21]

  - nominal composition $K_{0.8}Fe_2Se_2$

  - prereacted FeSe and K pieces (purity 99.999%, Alfa Aesar) were put into the alumina crucible and sealed into the quartz tube under a partial pressure of argon.

  - the quartz tube was heated to 1030 °C, kept at this temperature for 3 h, and then slowly cooled to 730 °C at a rate of 6 °C/h.

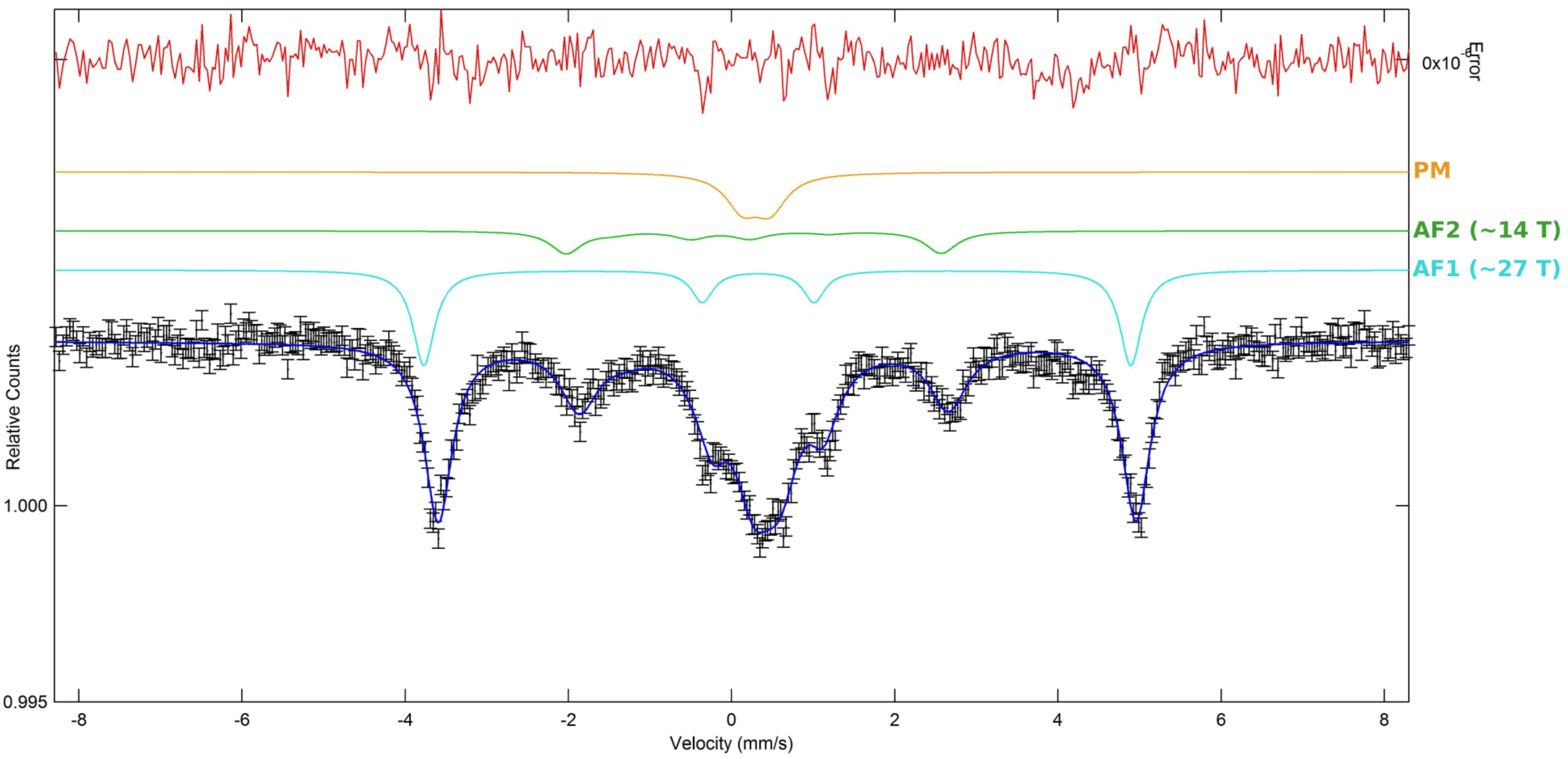
  - platelike crystals up to $5 \times 5 \times 1 mm^3$ were grown.

- XRD and SQUID measurements where done to check the structure and SC.

Results:

Mössbauer spectroscopy of KFe_2Se_2

- spectra recorded with Wissel Mössbauer system on room temperature
- ^{57}Co Mössbauer source in Rh-matrix (50 mCi / 1.85 GBq)
- textured sample (deviation from 3:2:1:1:2:3 sextet ratio)
- fitted subspectras with WinNormos-for-Igor



Results: *Calculations*

	KFe_2Se_2			$RbFe_2Se_2$		
	I4/mmm	**I4/m** $\sqrt{5} \times \sqrt{5}$	**I4/m** $\sqrt{2} \times \sqrt{2}$	**I4/mmm**	**I4/m** $\sqrt{5} \times \sqrt{5}$	**I4/m** $\sqrt{5} \times \sqrt{5}$ charged +1
HFF [T]	18.6	22	17 22	18.4	21.8	22.9
EFG [V/m²]	-0.51 x 10^{21}	2.79 x 10^{21}	4 x 10^{21} 1 x 10^{21}	-0.43 x 10^{21}	2.80 x 10^{21}	3.30 x 10^{21}
η	0.06	0.85	0.80 0.78	0.40	0.87	0.73
MM	2.39 μ_B	2.92 μ_B	2.71 μ_B 2.85 μ_B	2.41 μ_B	2.89 μ_B	2.96 μ_B
Atomic distances [Å]	Fe-Se: 2.421 Fe-Fe: 2.760 Se-K: 3.455	Fe-Se: 2.414 Fe-Se: 2.445 Fe-Se: 2.452 Fe-Se: 2.511 Fe-Fe: 2.695 Fe-Fe: 2.919		Fe-Se: 2.424 Fe-Fe: 2.771 Se-Rb: 3.502	Fe-Se: 2.409 Fe-Se: 2.425 Fe-Se: 2.432 Fe-Se: 2.491 Fe-Fe: 2.690 Fe-Fe: 2.921	Fe-Se: 2.405 Fe-Se: 2.429 Fe-Se: 2.433 Fe-Se: 2.493 Fe-Fe: 2.684 Fe-Fe: 2.924

Summary

- confirmed “phase separation”
- Mössbauer spectroscopy can be used to detect multiple phases in AFe_2Se_2
  → two magnetic Fe-sites on room temperature
  HFF: 14 T and 27 T
  → one PM site
- this is in accordance with multiple neutron diffraction measurements [7,9,11]
- hyperfine parameters from the calculations are in good agreement with Mössbauer spectroscopy ($\sqrt{5} \times \sqrt{5}$ and $\sqrt{2} \times \sqrt{2}$)
- $\sqrt{2} \times \sqrt{2}$ AFM the best candidate for parent of a SC phase
- good agreement with previous calculation works [22,23]
- excellent agreement of bondlengts values with EXAFS experiment[18]
  → Fe–Se bondlengths highly covalent
  → Fe–Fe bondlength with much smaller force constant compared to the binary FeSe.
- local relaxation of the Fe–Fe bondlength
  → compression of the FeSe unit
- anisotropy in KFe_2Se_2 results from the Fe-vacancies.
- the $K_xFe_2Se_2$ recalls the oxygen ordering effects on the superconductivity of cuprates [24,25]

Thank You !!!

References

[1] Komihara et al., J. Am. Chem. Soc. 2008, 130, 3296-3297
[2] Guo et al., Phys. Rev. B 82, 180520(R) 2010
[3] Ding et al., Nature Communications 4, 1897, (2013).
[4] Ricci et al., Supercond. Sci. Technol. 24 082002 (2011)
[5] Liu et al., Phys. Rev. B 92, 059901 (2015)
[6] Lazarević et al., Phys. Rev. B 86, 054503 (2012)
[7] Sabrowsky et al., J. Magn. and Magne Materials 54 57 (1986) 1497-1498
[8] Bao et al., Chin. Phys. Lett. Vol. 28, No. 8 (2011) 086104
[9] Zhao et al., PRL 109, 267003 (2012)
[10] Mittal et al., Phys. Rev. B 87, 184502 (2013)
[11] Pomjakushin et al., J. Phys.: Condens. Matter 23 (2011) 156003 (4pp)
[12] Ye et al., PRL 107, 137003 (2011)
[13] Chen et al., Phys. Rev. X 1, 021020 (2011)
[14] Li et al., Nature Physics 8, 126–130 (2012)
[15] Nowik et al., Supercond. Sci. Technol. 24 (2011) 095015 (6pp)
[16] Ryan et al., Phys. Rev. B 83, 104526 (2011)
[17] Ksenofontov et al., Phys. Rev. B 84, 180508(R) (2011)
[18] Iadecola et al., J. Phys.: Condens. Matter 24 (2012) 115701 (6pp)
[19] Shoemaker et al., Phys. Rev. B 86 184511 (2012)
[20] Yang et al., PRL 106, 087005 (2011)
[21] Hechang Lei and C. Petrovic., Phys. Rev. B 83, 184504 (2011)
[22] Yan et al., PRL 106, 087005 (2011)
[23] C. Cao and J. Dai, PRL 107, 056401 (2011)
[24] Fratini et al., Nature 466 841 (2010)
[25] Poccia et al., J. Supercond. Novel Magn. 24 1195–200 (2011)
[26] Qian T et al.,Phys. Rev. Lett. 106 187001 (2011)
[27] Zhang Y et al Nat. Mater. 10 273 (2011)
[28] Zhao et al., Phys. Rev. B 83 140508 (2011)