Lomonosov Moscow State University

Trilateral workshop on Hot Topics in HTSC: Fe-Based Superconductors

New members of Fe-based superconducting family AxFe2-ySe2: synthesis, microstructure and properties

Zvenigorod,
September 29 – October 2, 2013

Outline

I. Introduction

II. A comparative study of the microstructure of the superconducting and non-superconducting samples **$Rb_xFe_{2-y}Se_2$**

III. Synthesis and study of the properties ferroselenids **$(Na,K)_xFe_{2-y}Se_2$** with partial substitution of K by Na.

IV. Synthesis of ferroselenids **$A_x(C_5H_5N)_yFe_{2-z}Se_2$ (A=Li, Na)** by intercalation of lithium and sodium to FeSe in pyridine.

Classification of layered Fe-containing superconductors

Family	Parent compound	Substi-tution	Examples	T_c max, K
1111	***RE*OFeAs** *RE*=La,Ce,Pr,Nd,Sm,Tb,Dy ***AE*FFeAs**, *AE*=Ca, Sr	**O →F** ***AE*→*RE***	$LaO_{1-x}F_xFeAs$ $Ca_{1-x}La_xFFeAs$	55 36
122(As)	$AEFe_2As_2$ *AE*=Ca, Sr, Ba, Eu	***AE*→*A*** **Fe→Co** **As→P** ***AE*→*RE***	$Ba_{1-x}K_xFe_2As_2$ $SrFe_{1.7}Co_{0.3}As_2$ $BaFe_2(As_{2/3}P_{1/3})_2$ $Ca_{1-x}La_xFe_2As_2$	38 30 33 47
122(Se)	$A_{0.8}Fe_{1.6}Se_2$ *A*= alkali and alkaline earth metals		$K_xFe_{2-y}Se_2$ $Li_x(NH_2)_y(NH_3)_{1-y}Fe_2Se_2$ $Li_x(C_5H_5N)_yFe_{2-z}Se_2$	31 44 44
111	**LiFeAs,** **NaFeAs**	 **Fe→Co**	**LiFeAs,** $Na_{1-x}(Fe,Co)As$	18 23
11	**FeSe**	**Se→Te**	$Fe_{1+x}Se$ $FeSe_{0.4}Te_{0.6}$	9 15

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122(As)	$AEFe_2As_2$ *AE*=Ca, Sr, Ba, Eu	***AE*→*A*** **Fe→Co** **As→P** ***AE*→*RE***	$Ba_{1-x}K_xFe_2As_2$ $SrFe_{1.7}Co_{0.3}As_2$ $BaFe_2(As_{2/3}P_{1/3})_2$ $Ca_{1-x}La_xFe_2As_2$	38 30 33 47
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Key features of 122(FeSe) family

1) Variable composition with a deficit in the cation sublattices of iron and alkali metal:

$A_xFe_{(2-y)}Se_2$, where A - alkali metal or Tl, $0.6<x<1$, $1.5<(2-y)<1.7$

2) The formal oxidation state of iron in SC-samples is close to **2**. This means that with increasing iron content (2-y) the alkali metal content x decreases, and vice versa.

3) Depending on the composition, synthesis conditions and temperature measurements can be realized different micro-(nano)structures as a result of different ways of ordering the iron and alkali metal.

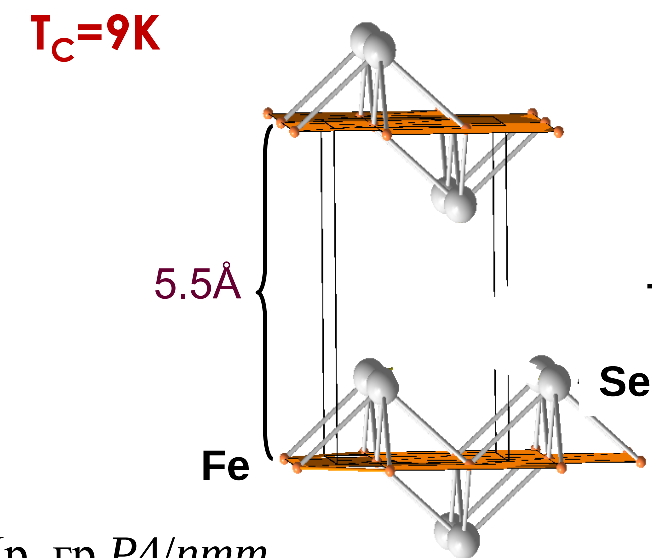
4) Parent compound for $A_xFe_{2-y}Se_2$ family is

$$A_{0.8}Fe_{1.6}Se_2 \equiv A_2Fe_4Se_5$$

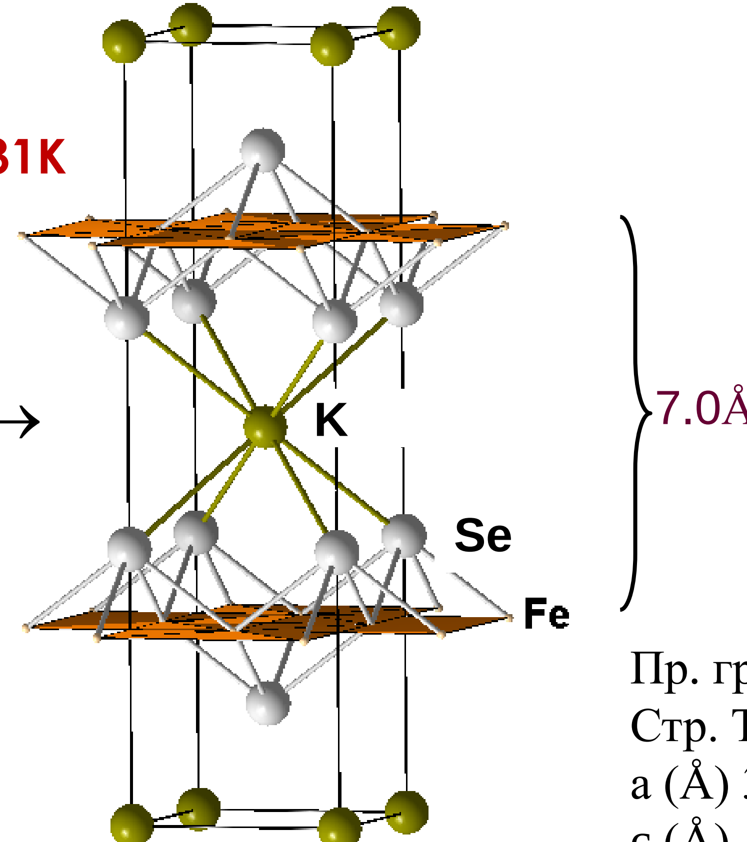
20% of Fe and K atomic positions are empty. As rule substances with small deviation from this composition may be superconductors.

Synthesis of $A_xFe_{2-y}Se_2$ by intercalation of t-FeSe

[J.Guo, S.Jin, G. Wang, et al PRB, 82, 180520R (2010)]



+ K →



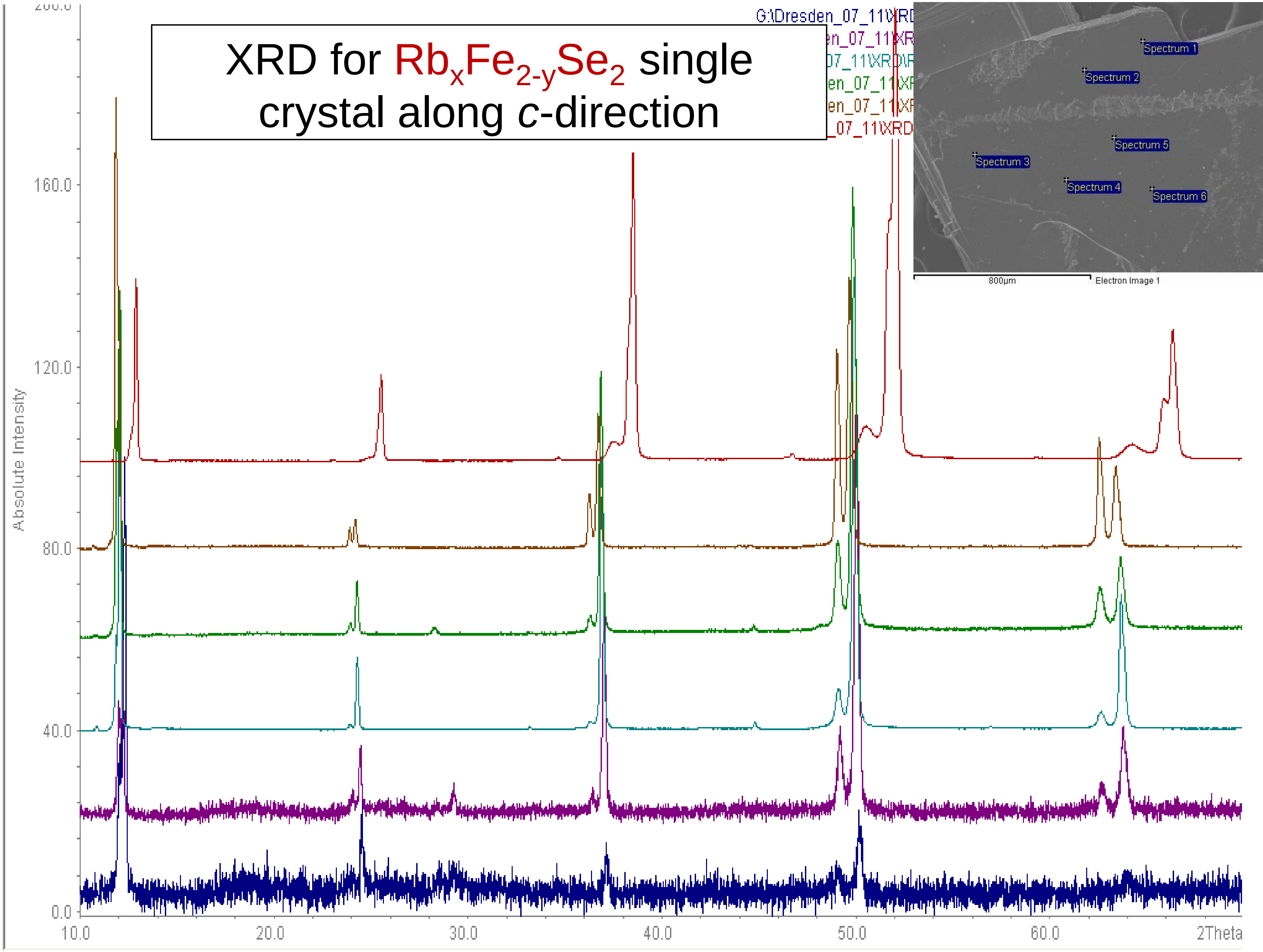
Пр. гр.*P4/nmm*
Стр. Тип *анти*-PbO
a (Å) 3.77376(2)
c (Å) 5.52482(5)

Пр. гр.*I4/mmm*
Стр. Тип $ThCr_2Si_2$
a (Å) 3.9136(1)
c (Å) 14.0367(7)

Synthesis by "self-flux" technique:

(2FeSe+0.8K) in double quarts tube, heating up to 1030-1070^{o}C, short dwell (2-5hs) and cooling with the rate about 5-6^{o}C up to 750^{o}C

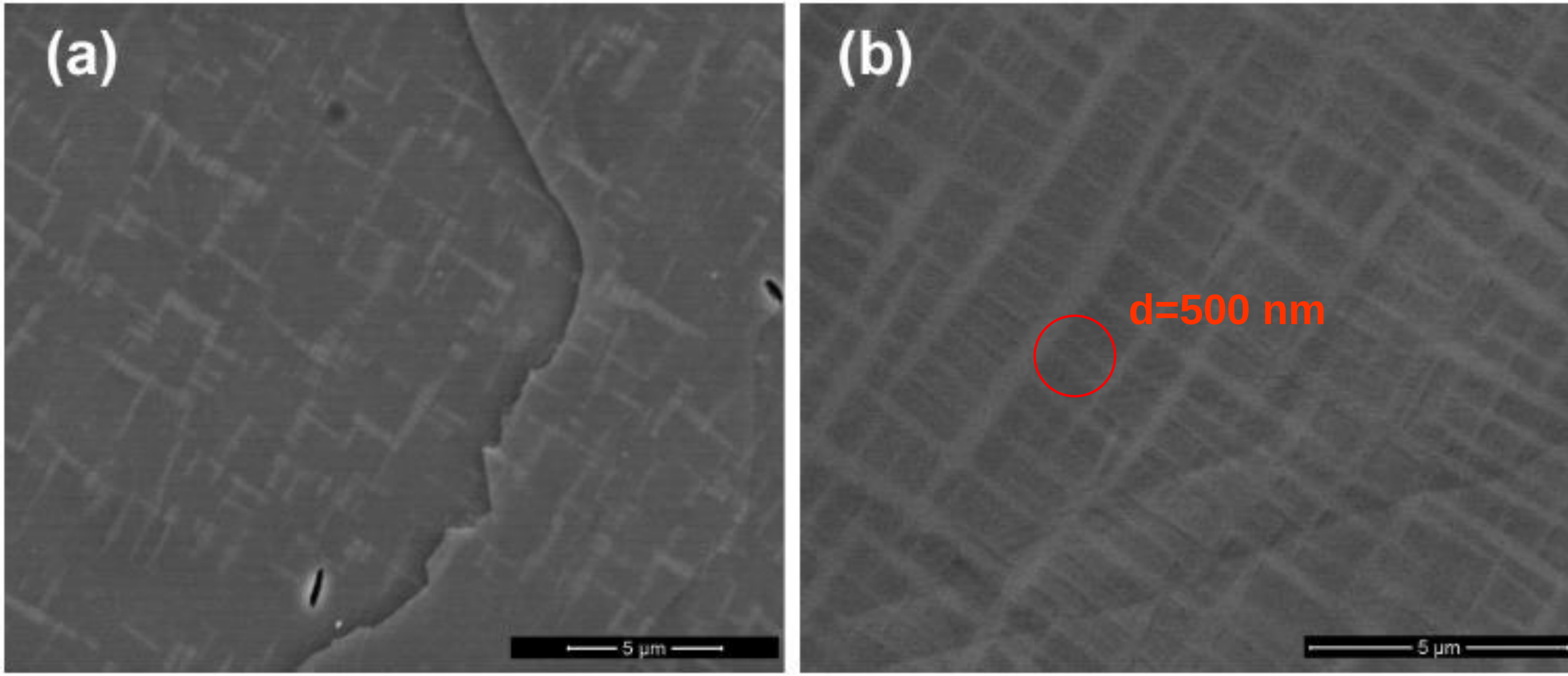
XRD for $Rb_xFe_{2-y}Se_2$ single crystal along *c*-direction



SEM and EDX

The SC sample (Tc 24K) | The non-SC sample

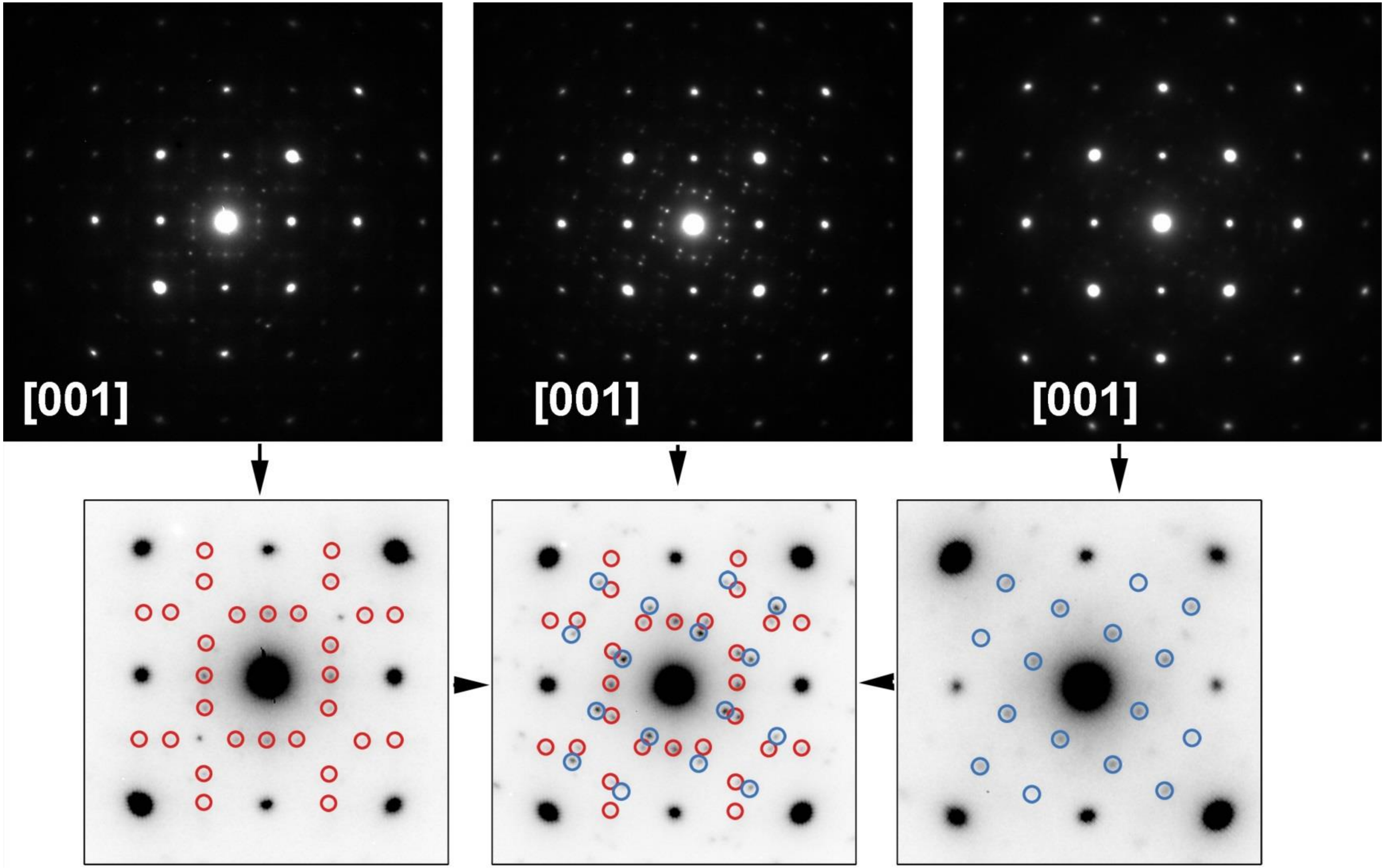
$Rb_{0,73(6)}Fe_{1,72(4)}Se_2$ | $Rb_{0,75(1)}Fe_{1,66(3)}Se_2$



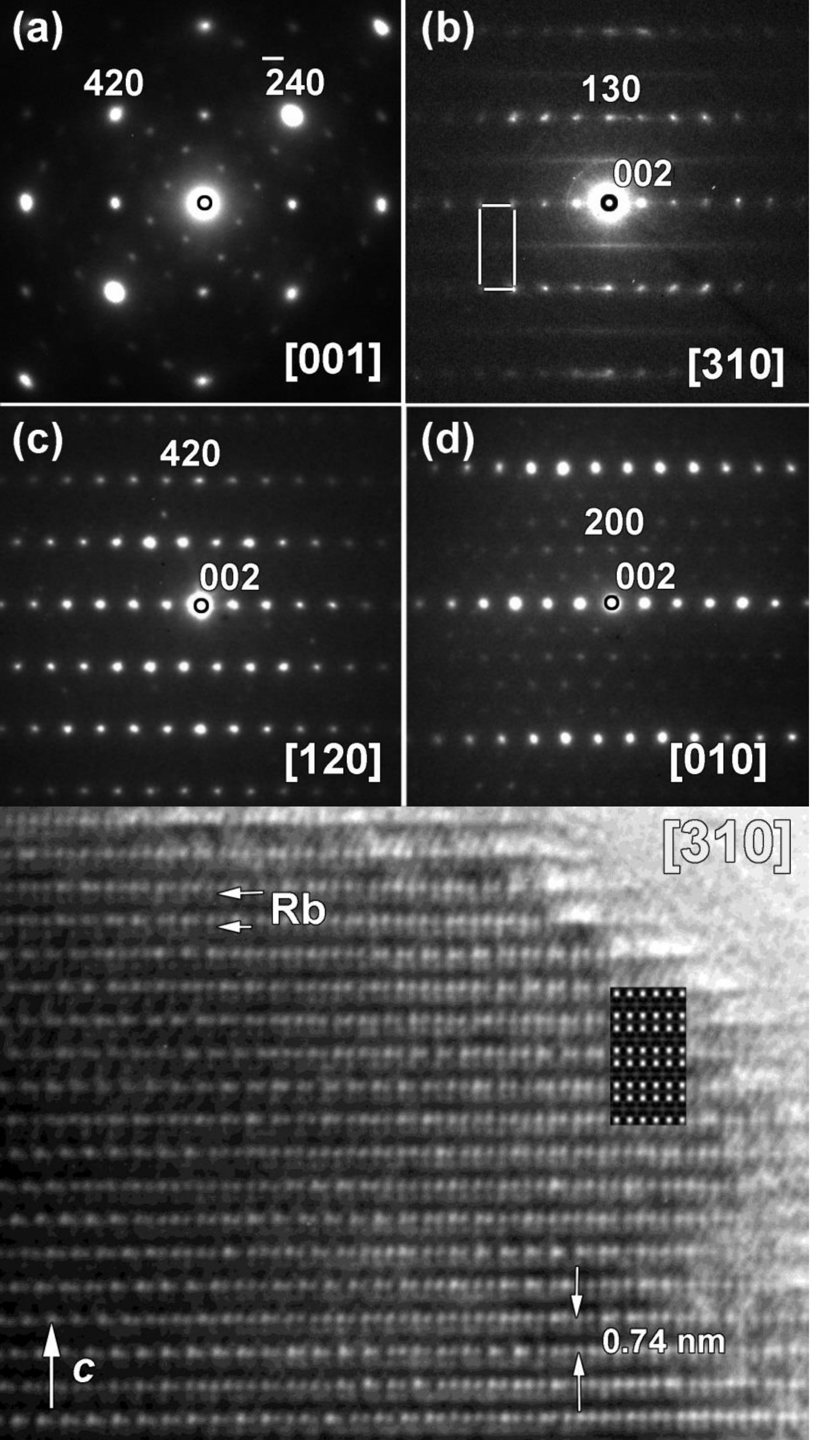
The phase contrast indicates a microinhomogeneity of the samples

Thus, in this work we solved the problem of a detailed study of the microstructure of the superconducting and non-superconducting sample $Rb_xFe_{2-y}Se$ to identify the structural features responsible for the superconducting properties.

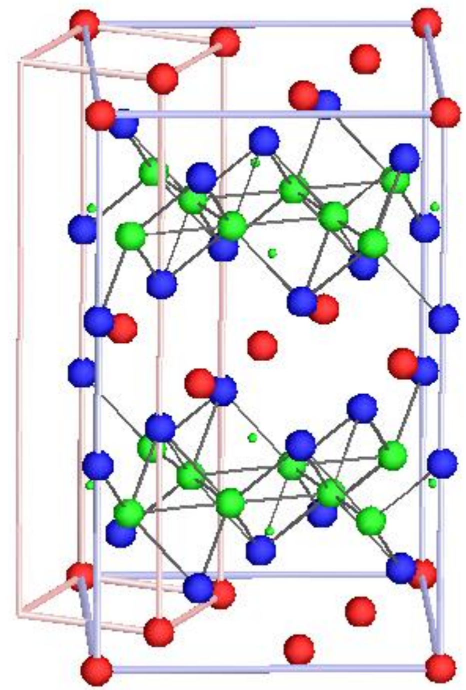
The variety of superstructures in the [001] zone-axis direction



ordering of type II **Mixture of types I and II** **ordering of type I**



Superstructure I: the well-known Fe vacancy-ordered structure (space group I4/m)

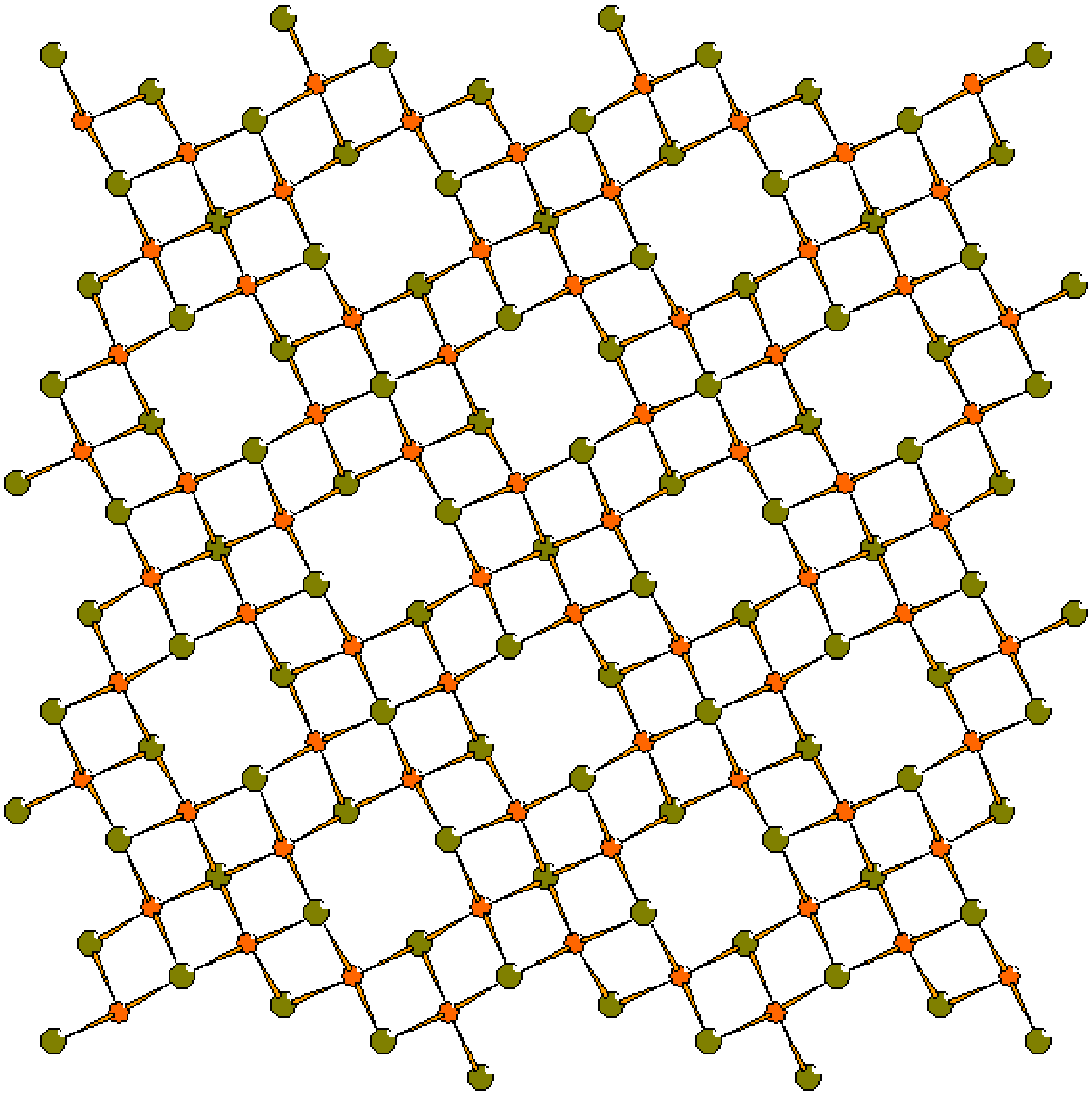


$a_I = 2a_S + b_S$
$b_I = -a_S + 2b_S$
$c_I = c_S$

$a_I = b_I = a_S\sqrt{5} \approx 8.7$ Å
$c_I = 14.5$ Å

$K_{0.8}Fe_{1.6}Se_2$: 1/5 part of Fe atoms absent.

Ordered structure: Space group *I4/m* (T< 580 K)

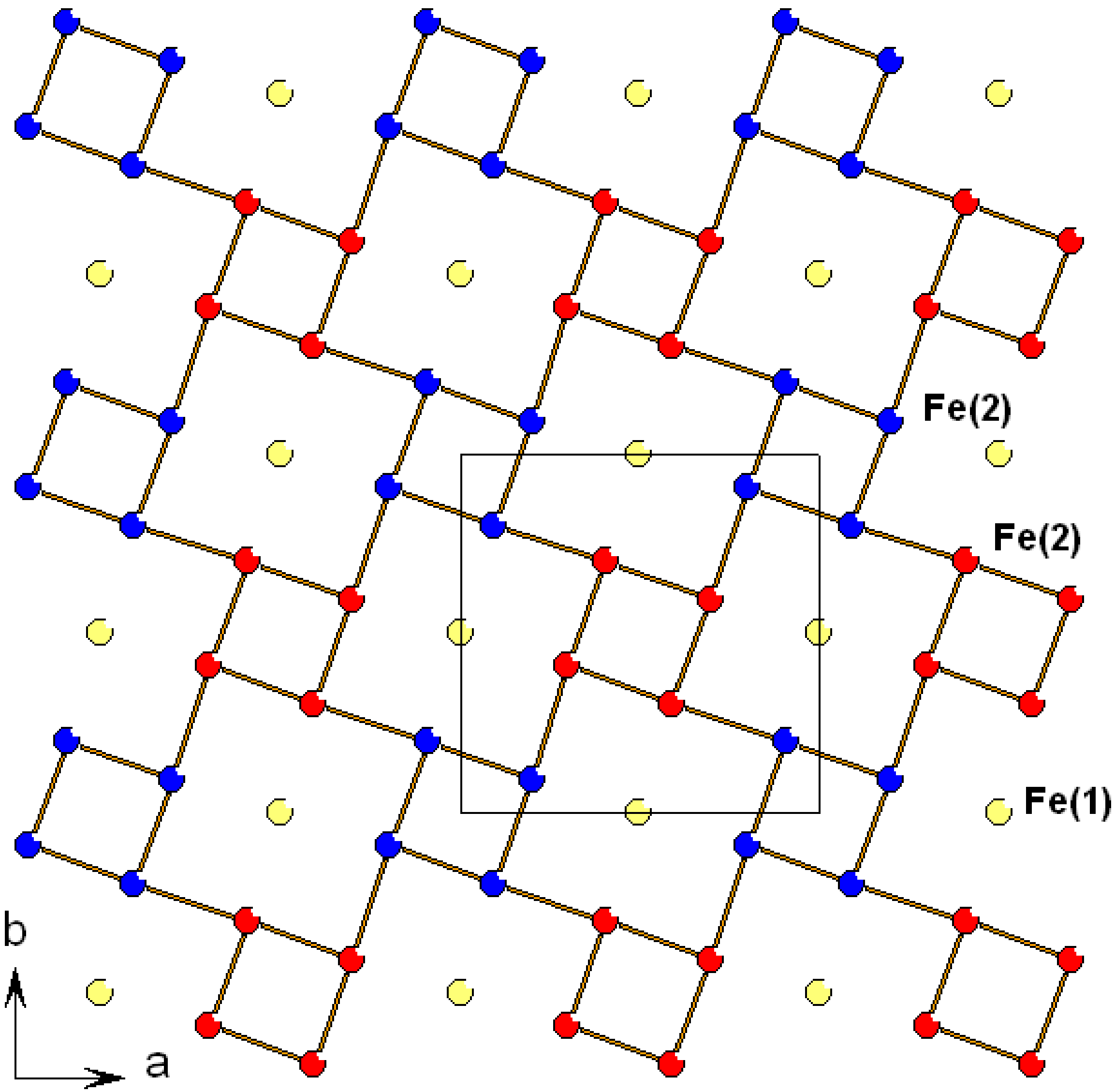


With decreasing temperature, the ordering of vacancies occur.

Legend:

- **Fe**
- **As**

$K_{0.8\pm x}Fe_{1.6\pm y}Se_2$ *I4/m* structure: antiferromagnetic ordering at the T_N< 560 K



For clarity, only Fe atoms in one layer (without Se) are shown

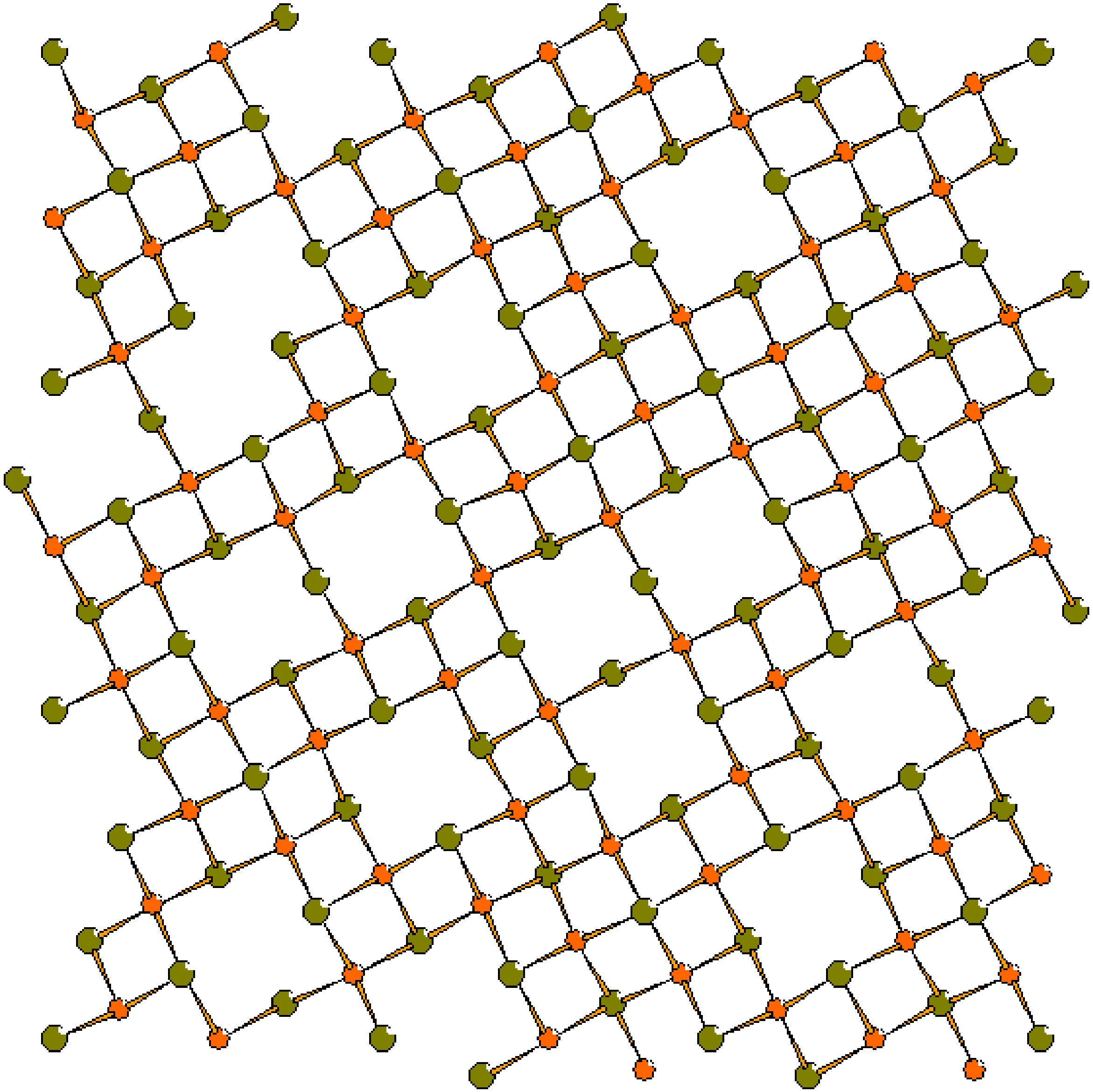
[Bao, W. et al. **2011**, arXiv:1102.3674] ***(Neutron powder diffraction)***

Legend:

● and ● - spin-up and spin-down configurations of Fe(2) atoms

$K_{0.8}Fe_{1.6}Se_2$: 1/5 part of Fe atoms absent.

Disordered structure: Space group *I4/mmm* (T>580 K)



At the temperature more than 570 – 600K vacancies of Fe atoms are distributed in layers without ordering.

This structure is very similar to the AFe_2As_2 stoichiometric compounds :

sp.gr. I4/mmm

a ≈ 4 Å

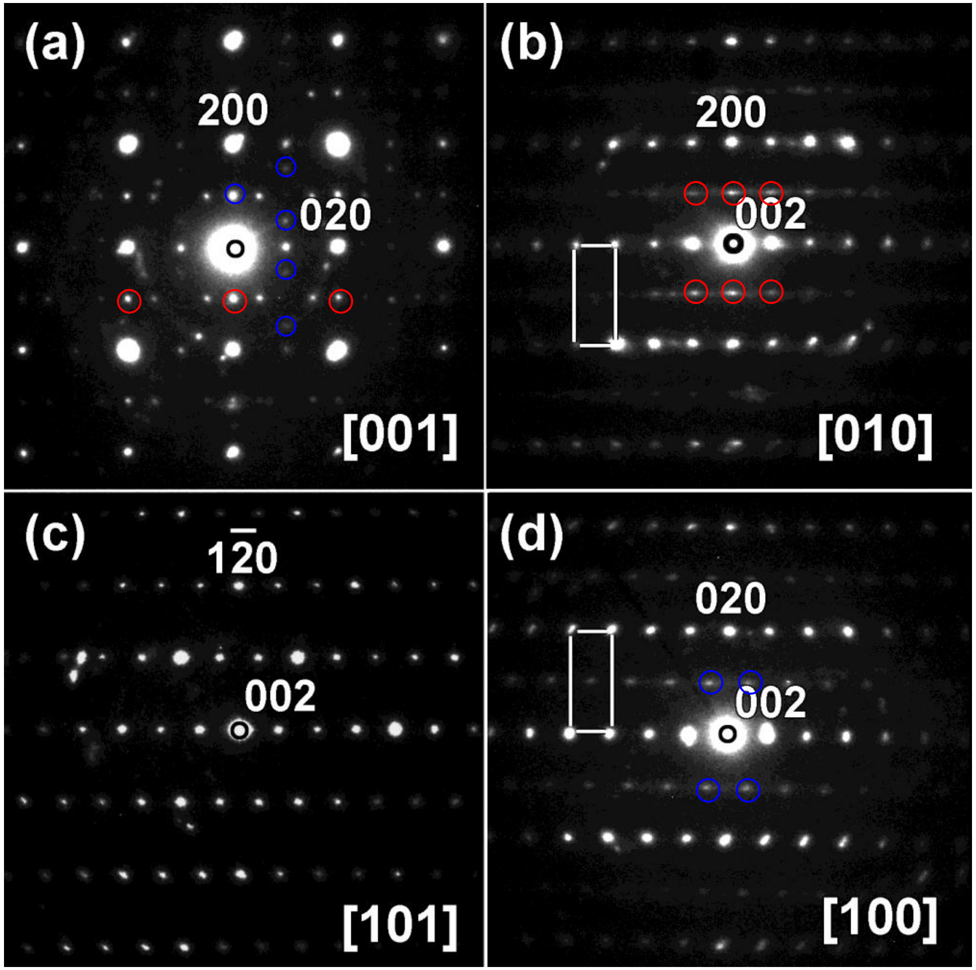
c ≈14 Å

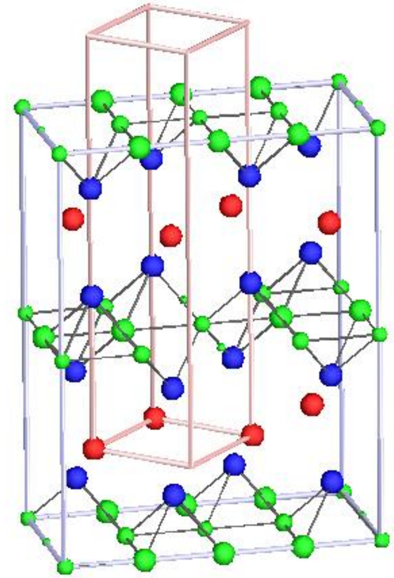
Legend:

- **Fe**

- **As**

Superstructures II and III with the ordered Fe and Rb vacancies



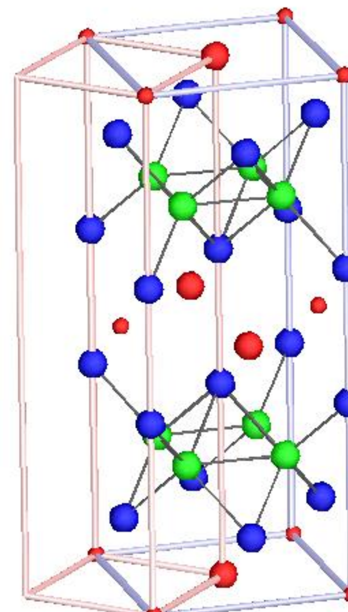


Fe ordering

$a_{II} = a_s + b_s$
$b_{II} = 2(a_s - b_s)$
$c_{II} = c_s$

Space group I222

$\mathbf{a_{II} = a_s\sqrt{2} \approx 5.5\ Å}$
$\mathbf{b_{II} = 2a_s\sqrt{2} \approx 11\ Å}$
$\mathbf{c_{II} = 14.5\ Å}$



Rb ordering

$a_{III} = a_s + b_s$
$b_{III} = a_s - b_s$
$c_{III} = c_s$

Space group Ammm

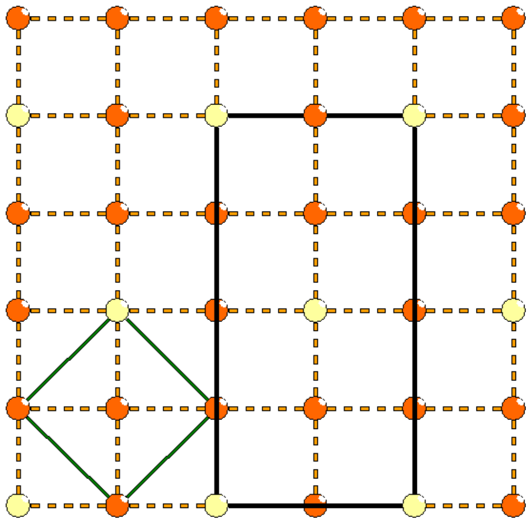
$\mathbf{a_{III} = a_s\sqrt{2} \approx 5.5\ Å}$
$\mathbf{b_{III} = a_s\sqrt{2} \approx 5.5\ Å}$
$\mathbf{c_{III} = 14.5\ Å}$

Different possibility for vacancy ordering for $A_1Fe_{1.5}Se_2$

$\sqrt{2} \times 2\sqrt{2}$ *Ibam*

a‘=√2a, b‘= 2√2a, c‘=c

a



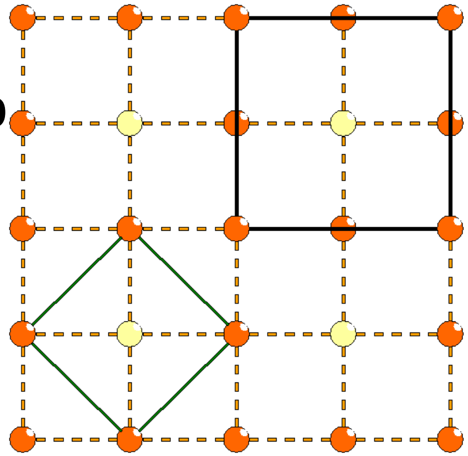
Реализуется в $Tl_2Fe_3S_4$

[PRL 106, 087005 (2011)]

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

a‘=b‘=√2a, c‘=c

b

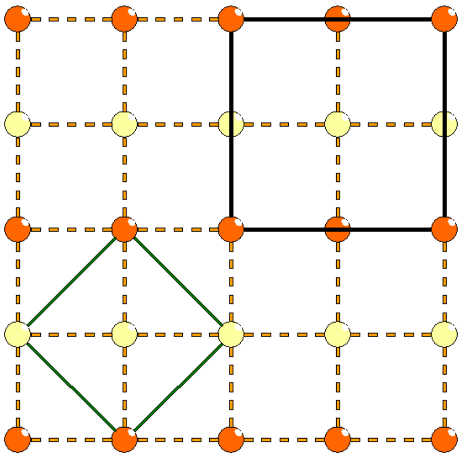


Предсказан для $A_2Fe_3Se_4$

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

a‘≈√2a, b‘≈√2a, c‘=c

c

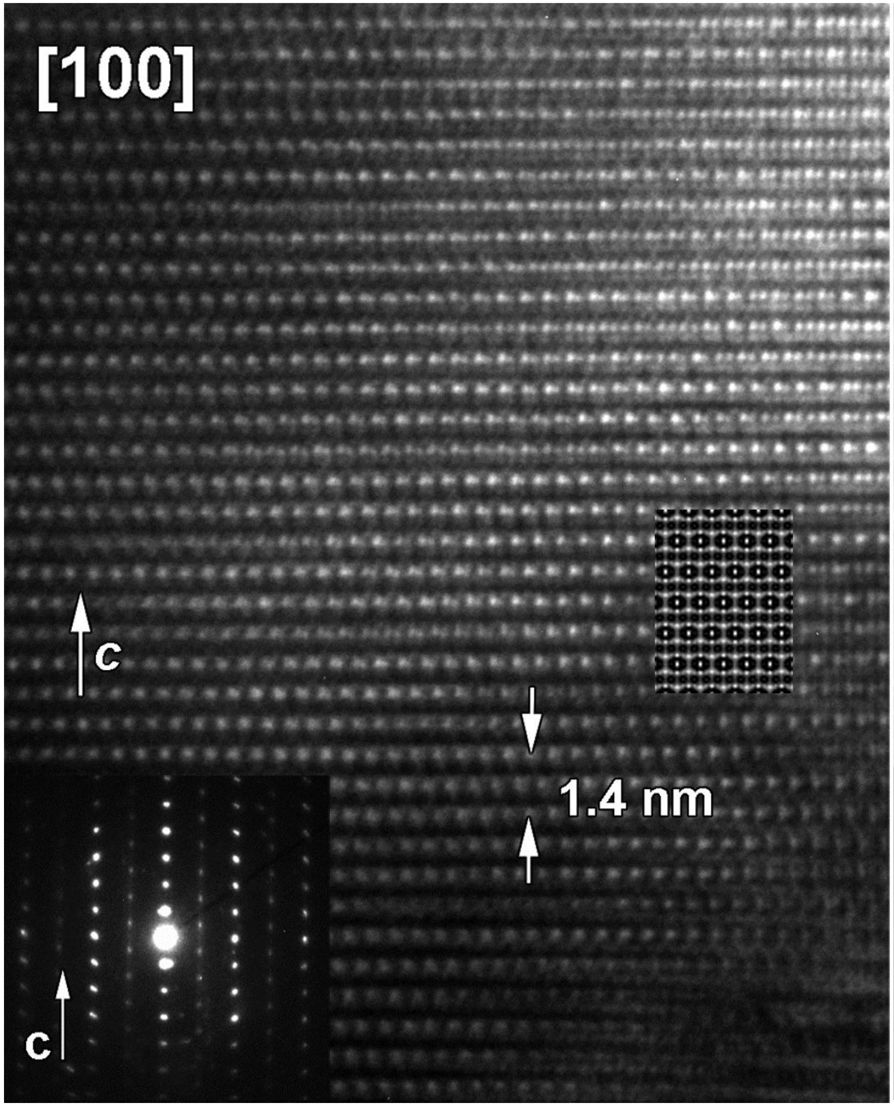


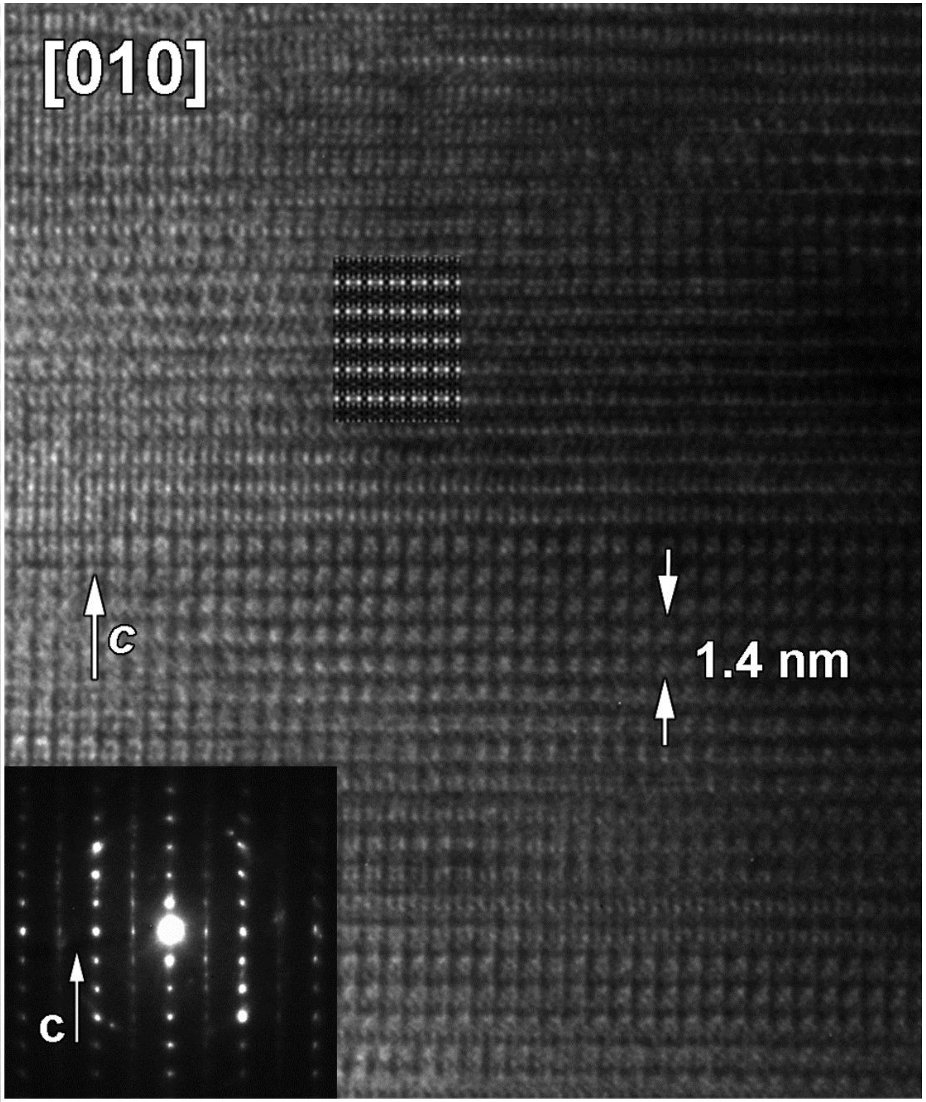
Реализуется в $KFe_{1.5}Se_2$

[arXiv:1102.3674v1].

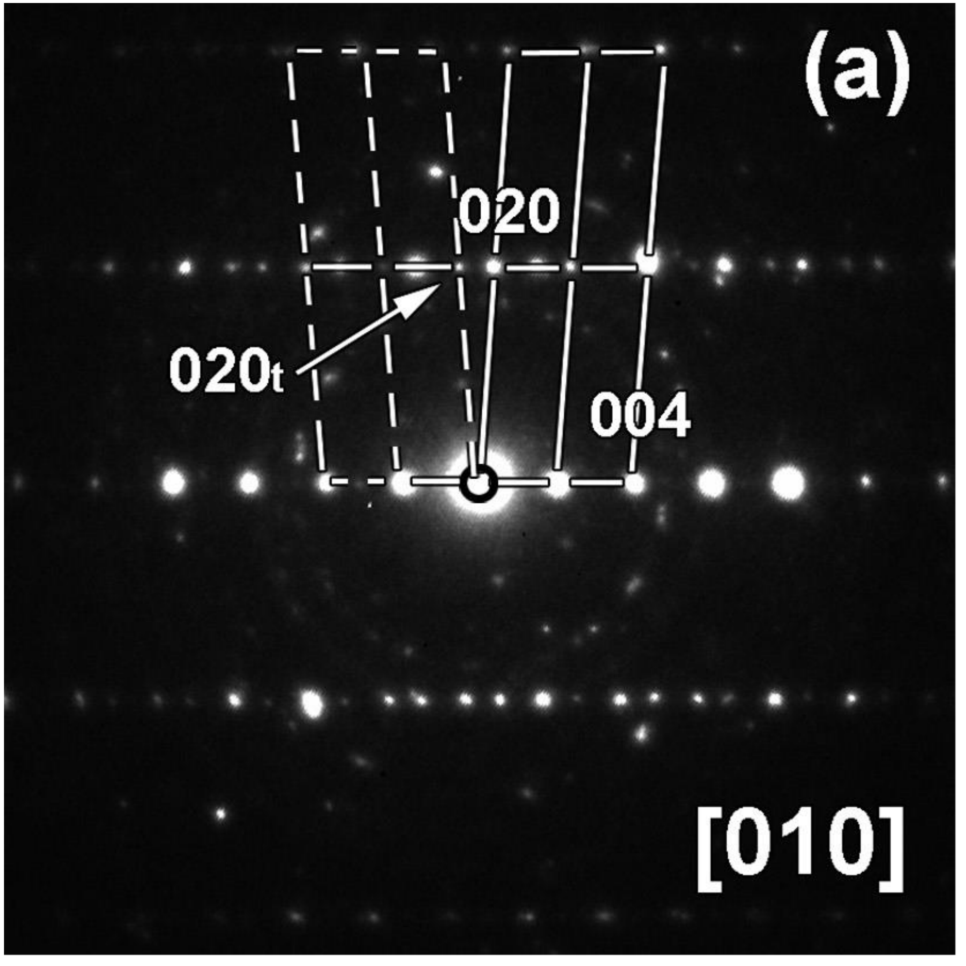
HRTEM study: SC sample

Structure model based on **Superstructure III** with Ammm space group and cell parameters a =b ≈5.5 Å, c = 14.5 Å

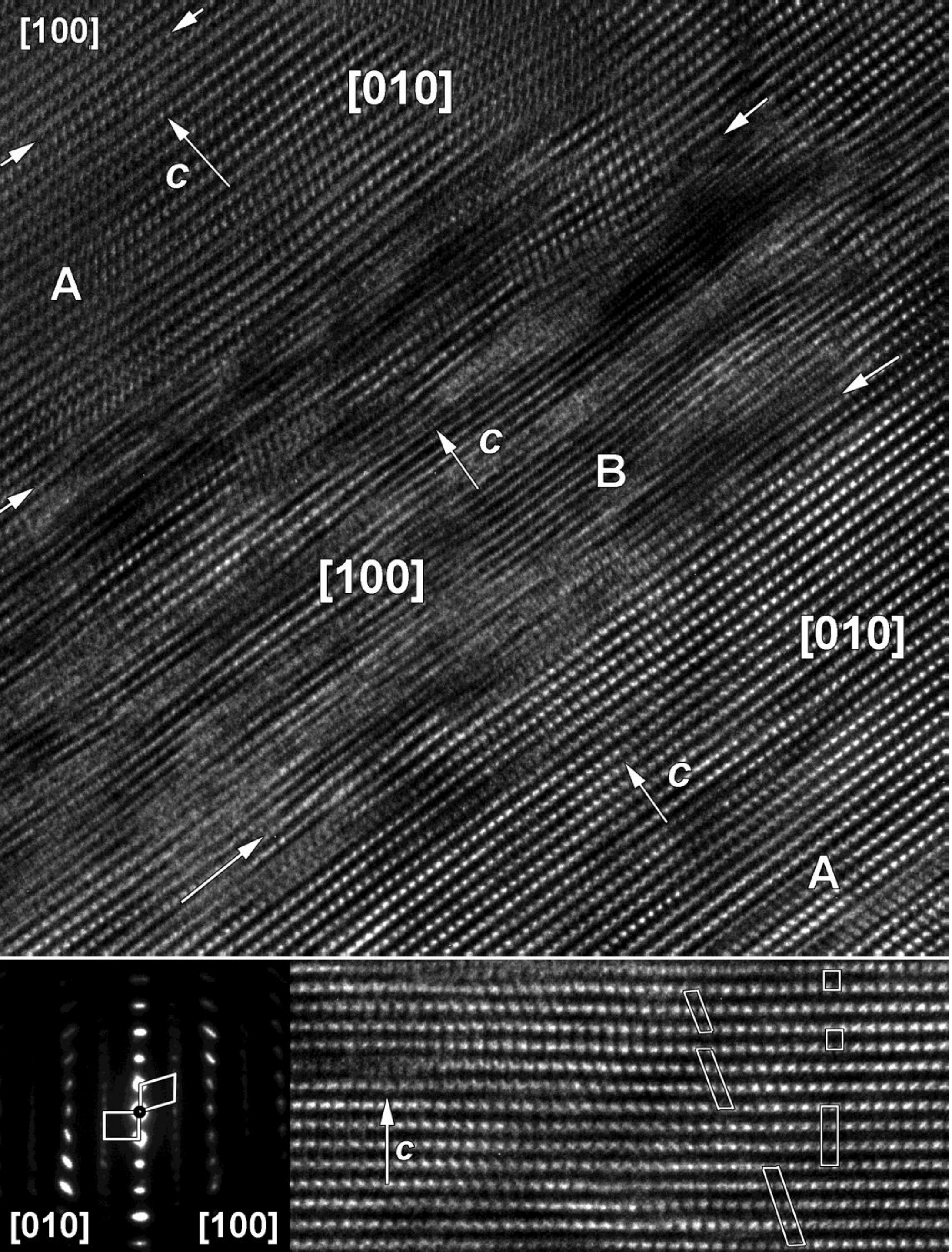


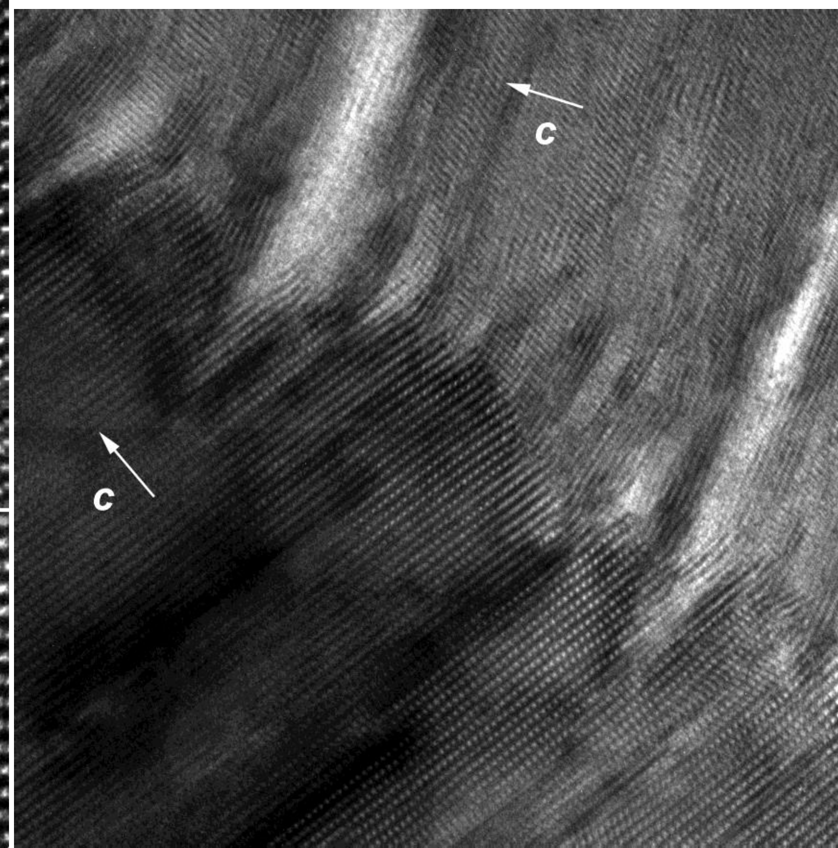


The monoclinic distortion in the SC-sample

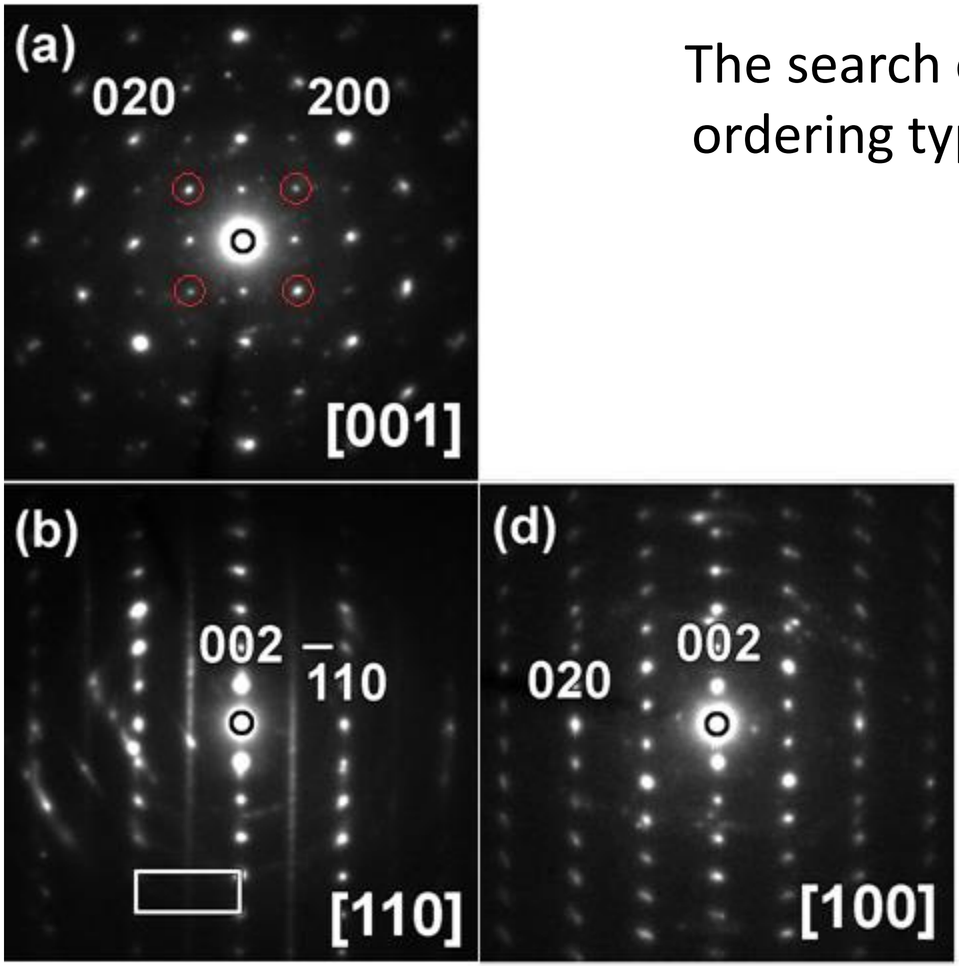


HRTEM study: Non-SC sample

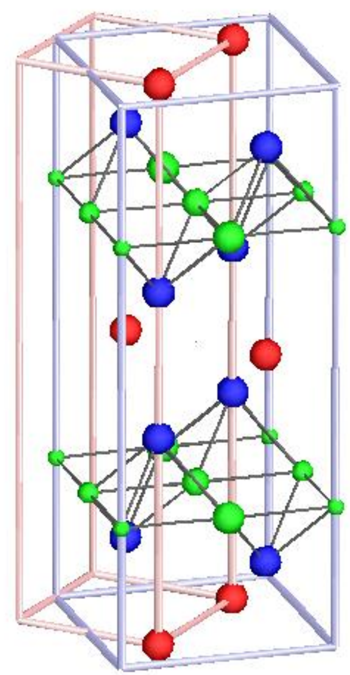




The structure features of non-SC $Rb_{0,75(1)}Fe_{1,66(3)}Se_2$



The search of the alternative Fe vacancy ordering types among the subgroups of I4/mmm



Pccm

$a=b=\sqrt{2}a_s=5.5Å$
$c=14.5Å$

Conclusions

1. For the first time the superconducting and the nonsuperconducting $Rb_xFe_{2-y}Se_2$ materials with close composition were investigated in detail by ED and TEM.

2. It is shown that the alternation of ordered and disordered regions is characteristic for both SC and non-SC materials.

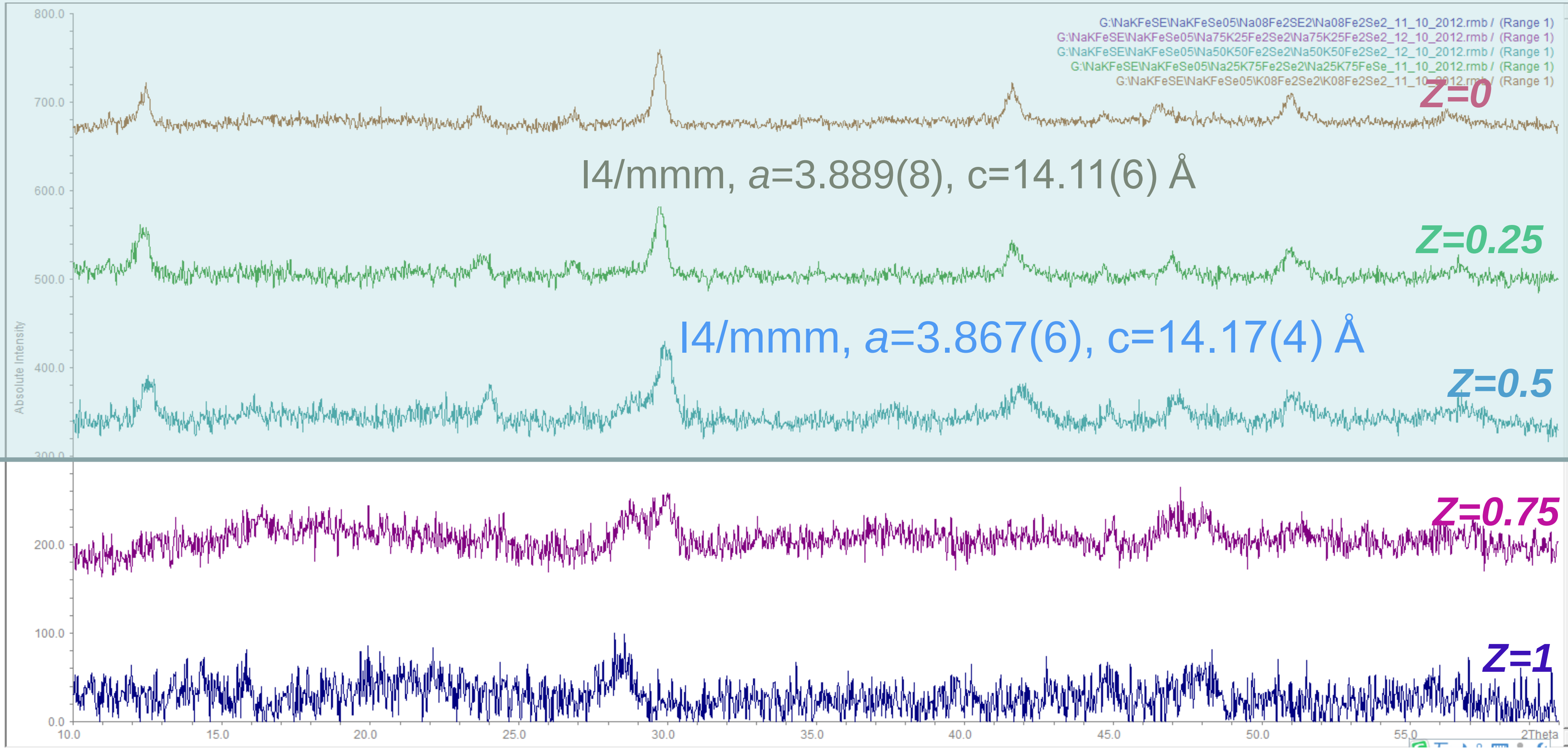
3. Three types of electron diffraction patterns were found for the superconducting $Rb_xFe_{2-y}Se_2$ sample, of which one is observed for the first time and originates from alkali metal ordering.

4. Moreover, for the superconducting $Rb_xFe_{2-y}Se_2$ material a monoclinic distortion with $\beta \sim 87^o$ was observed. This monoclinic distortion seems to be an attribute of the superconducting material only.

5. The non-superconducting sample the orthogonality of the crystallographic axes is preserved.

III. Synthesis and study of the properties of ferroselenids $(Na,K)_xFe_{2-y}Se_2$ with partial substitution of K by Na.

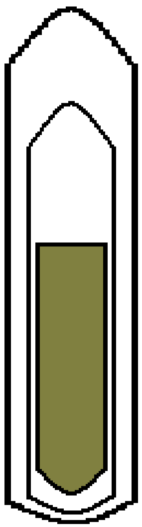
Synthesis of polycrystalline $(Na_zK_{1-z})_xFe_{2-y}Se_2$

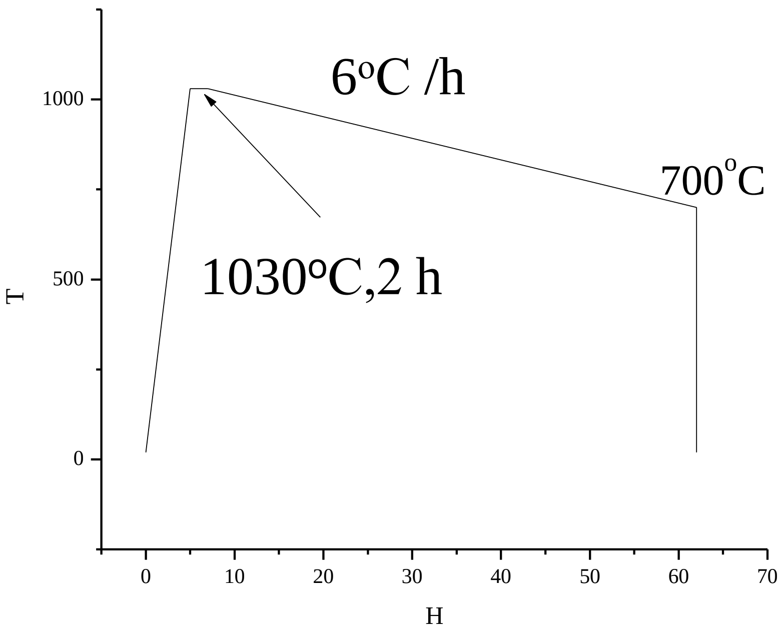


Synthesis of Single crystalline samples $(Na_zK_{1-z})_xFe_{2-y}Se_2$

1. Prereaction 0.8 A + 2FeSe $\longrightarrow$ «$A_{0.8}Fe_2Se_2$» **A= K, Na (**380°C 6 h)

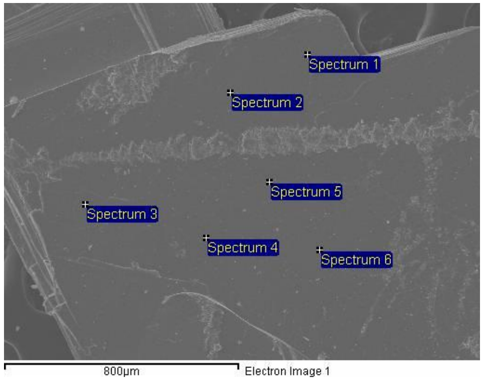
2)





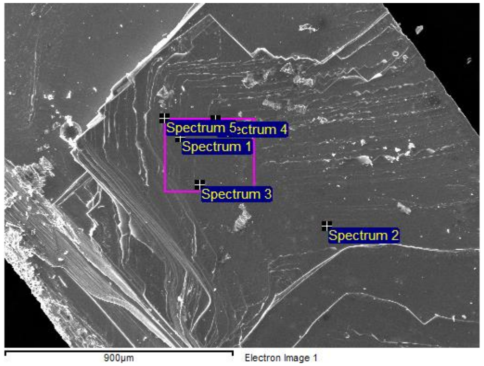
EDX

Z=0



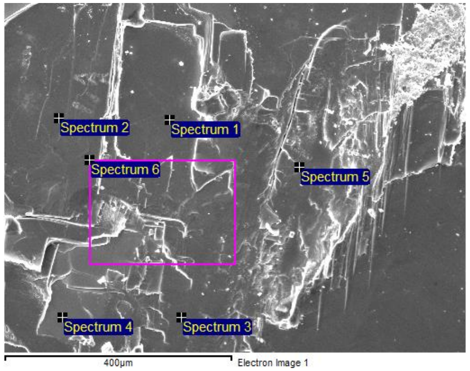
$K_{0,82(5)}Fe_{1,75(8)}Se_2$

Z=0.3



$(Na_{0.32(2)}K_{0.68(2)})_{0.95(4)}Fe_{1.75(2)}Se_2$

Z=0.4

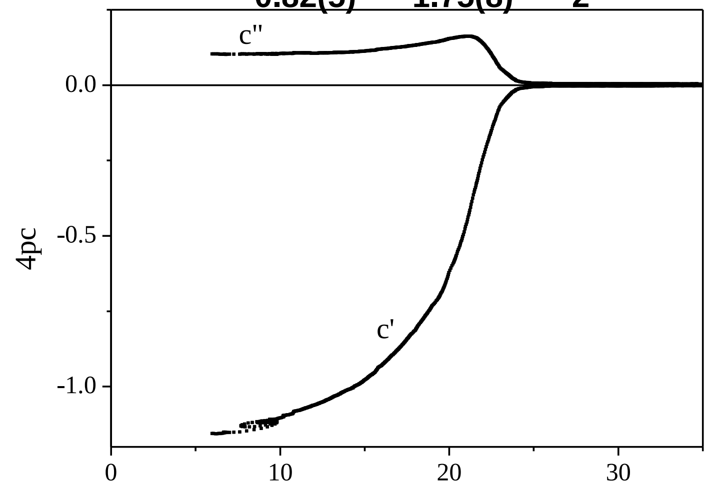


$(Na_{0.39(1)}K_{0.61(2)})_{0.97(4)}Fe_{1.78(2)}Se_2$

$(Na_{0.53(5)}K_{0.47(2)})_{0.73(3)}Fe_{1.88(1)}Se_2$

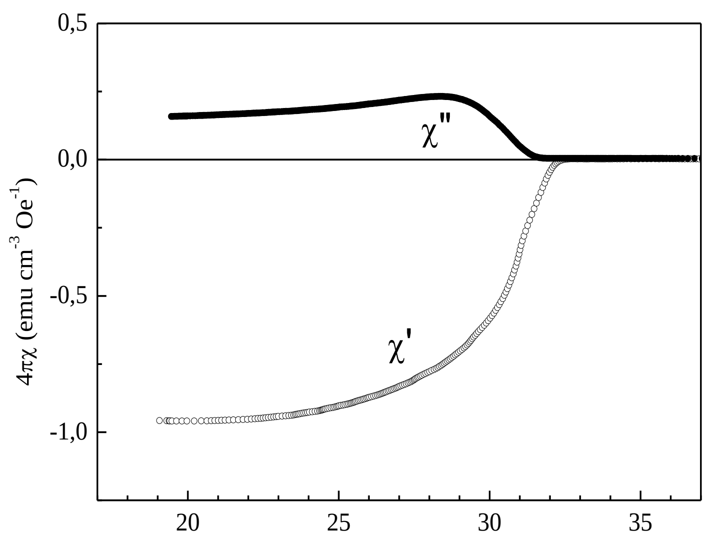
Magnetization measurements of $K_xFe_{2-y}Se_2$ and $(K,Na)_xFe_{2-y}Se_2$

$K_{0.82(5)}Fe_{1.75(8)}Se_2$

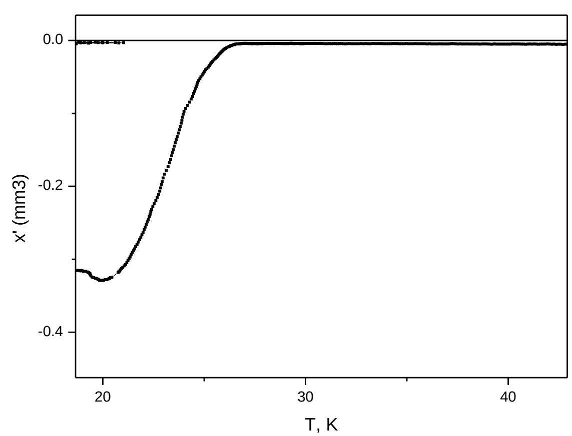


PCMA $(Na_zK_{1-z})_xFe_{2-y}Se_2$

$(Na_{0.32(2)}K_{0.68(2)})_{0.95(4)}Fe_{1.75(2)}Se_2$



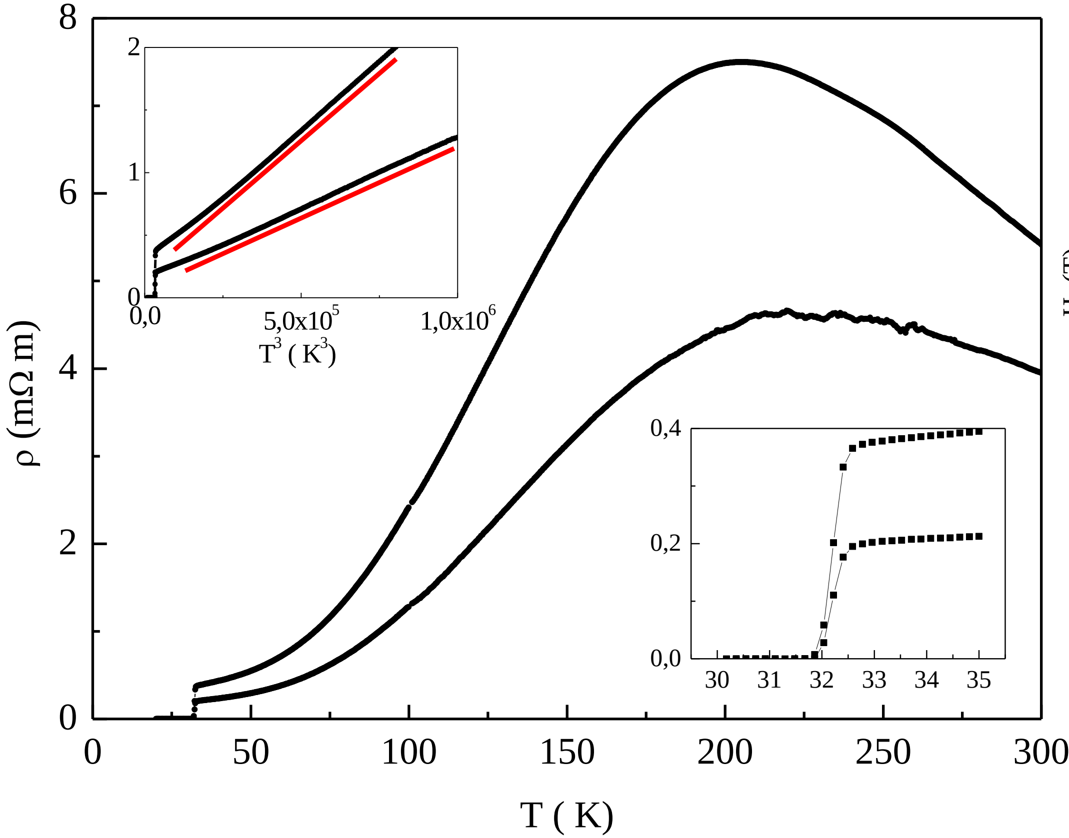
$(Na_{0.39(1)}K_{0.61(2)})_{0.97(4)}Fe_{1.78(2)}Se_2$

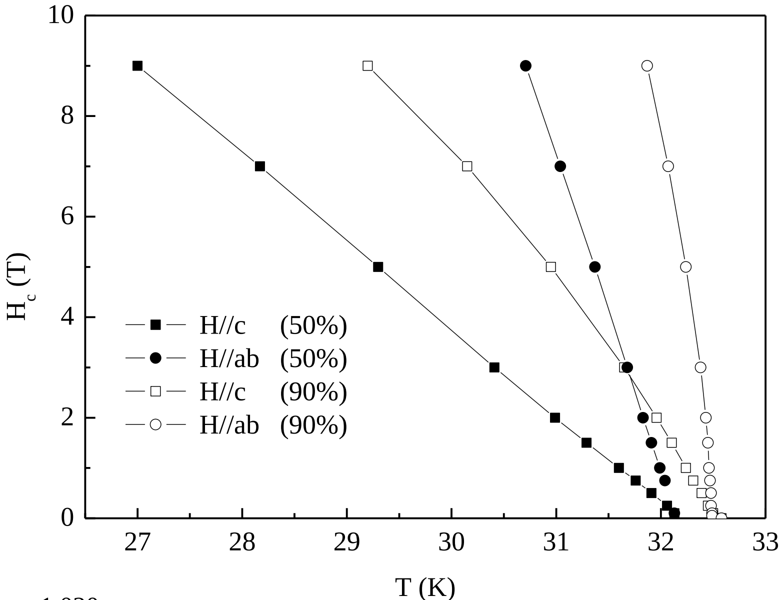


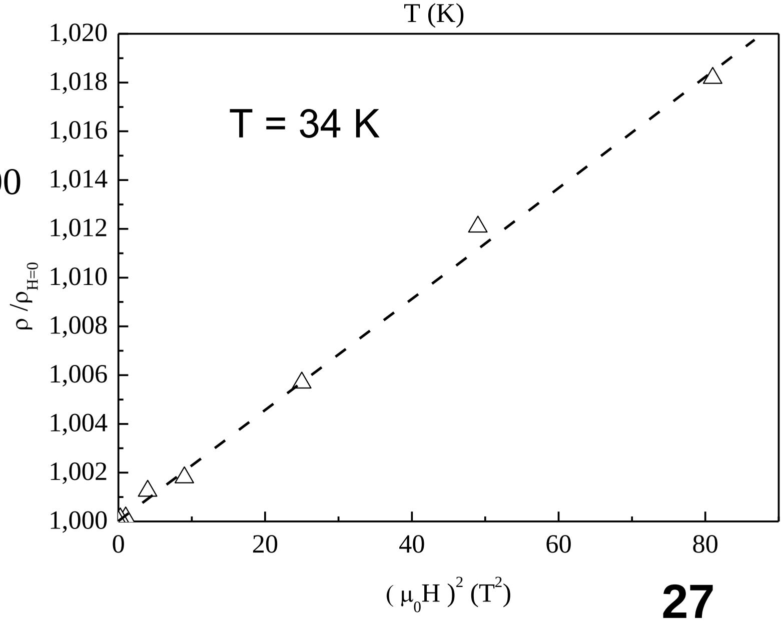
X-ray diffraction analisys $(Na_zK_{1-z})_xFe_{2-y}Se_2$

Z	Composition	Параметры Å		T_C K
		a	*c*	
0*	$Cs_xFe_{2-y}Se_2$	8,8582	15,2873	28.5
0**	$Rb_xFe_{2-y}Se_2$	8,799	14,576	31.5
0**	$K_{0.82(5)}Fe_{1.75(8)}Se_2$	8,73	14,115	29.5
0	$K_{0.82(5)}Fe_{0.75(8)}Se_2$	8.71(1)	14.11(2)	24
0.25***	$(Na_{0.21(4)}K_{0.79(2)})_{0.67(2)}Fe_{1.49(1)}Se_2$	8.67(2)	14.23(5)	31
0.3	$(Na_{0.32(2)}K_{0.68(2)})_{0.95(4)}Fe_{1.75(2)}Se_2$	8.72(2)	14.16(8)	32.4
0.4	$(Na_{0.39(1)}K_{0.61(2)})_{0.97(4)}Fe_{1.78(2)}Se_2$ $(Na_{0.53(5)}K_{0.47(2)})_{0.73(3)}Fe_{1.88(1)}Se_2$	8.725(6)	14.23(4)	26

Resistivity measurements of $(Na_{0.3}K_{0.7})_xFe_{2-y}Se_2$



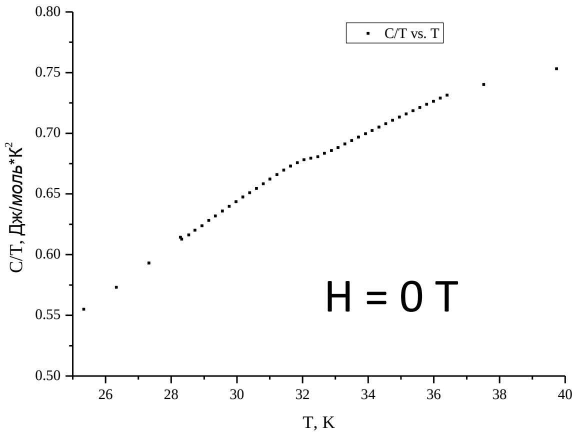


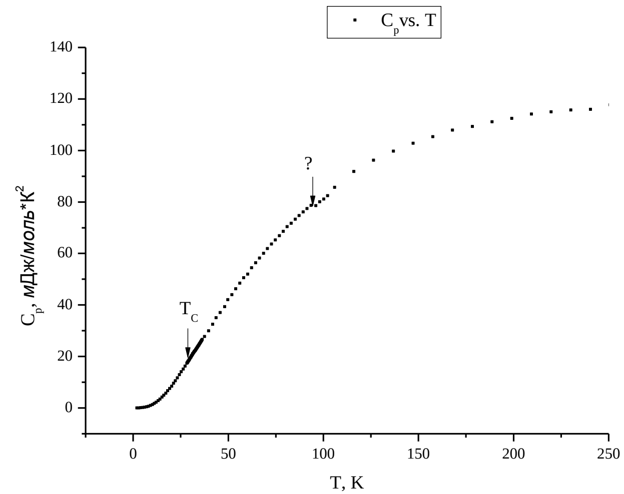


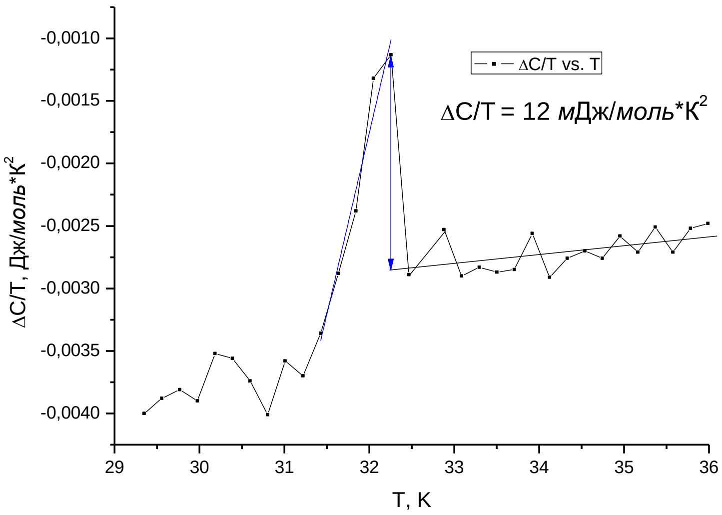
$-dH^{c}_{c2}/dT=24.8$ T/K
$-dH^{ab}_{c2}/dT=3.4$ T/K

positive transverse magnetoresistance ~ $H^{1/2}$

Specific heat measurements of $(Na,K)_xFe_{2-y}Se_2$





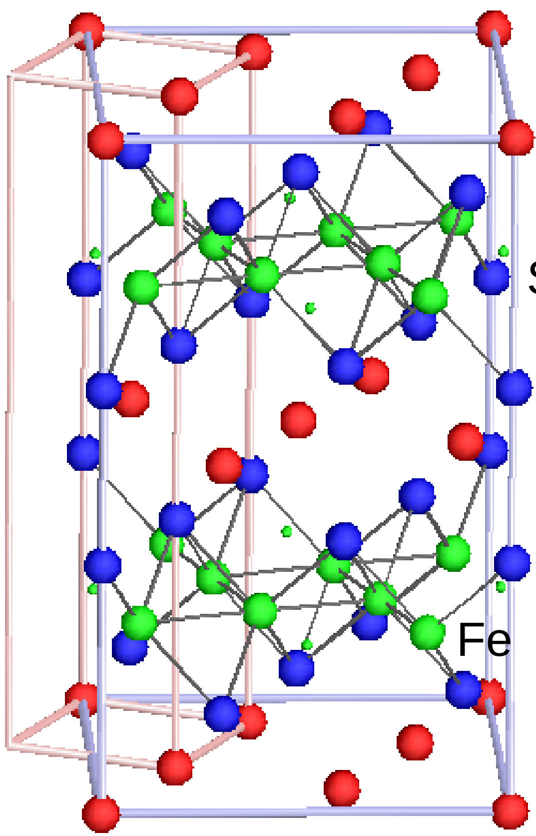


- There are 2 features on the specific heat curve: at T = 32 K (corresponds T_C), and at T = 95 K.
- The jump of C/T at $T=T_C$ is found to be ~12 mJ/mol*K^2.
- In the low temperature range the data can be fitted with the equation:

$$C_p(T) = \gamma T + \beta T^3$$

where γT – electron contribution, βT^3 – phonon contribution.
- γ at H=0 T is found to be ~0.4 mJ/mol*K^2

High-resolution X-ray diffraction study of $K_xFe_{2-y}Se_2$ and $(K_{0.7}Na_{0.3})_xFe_{2-y}Se_2$ using SR



HRXRD revealed the presence of at least two phases: $A_2Fe_4Se_5$ (s.g. I4/m) и $A_xFe_2Se_2$ (s.g. I4/mmm). The refinement of the cell parameters led to the following values:

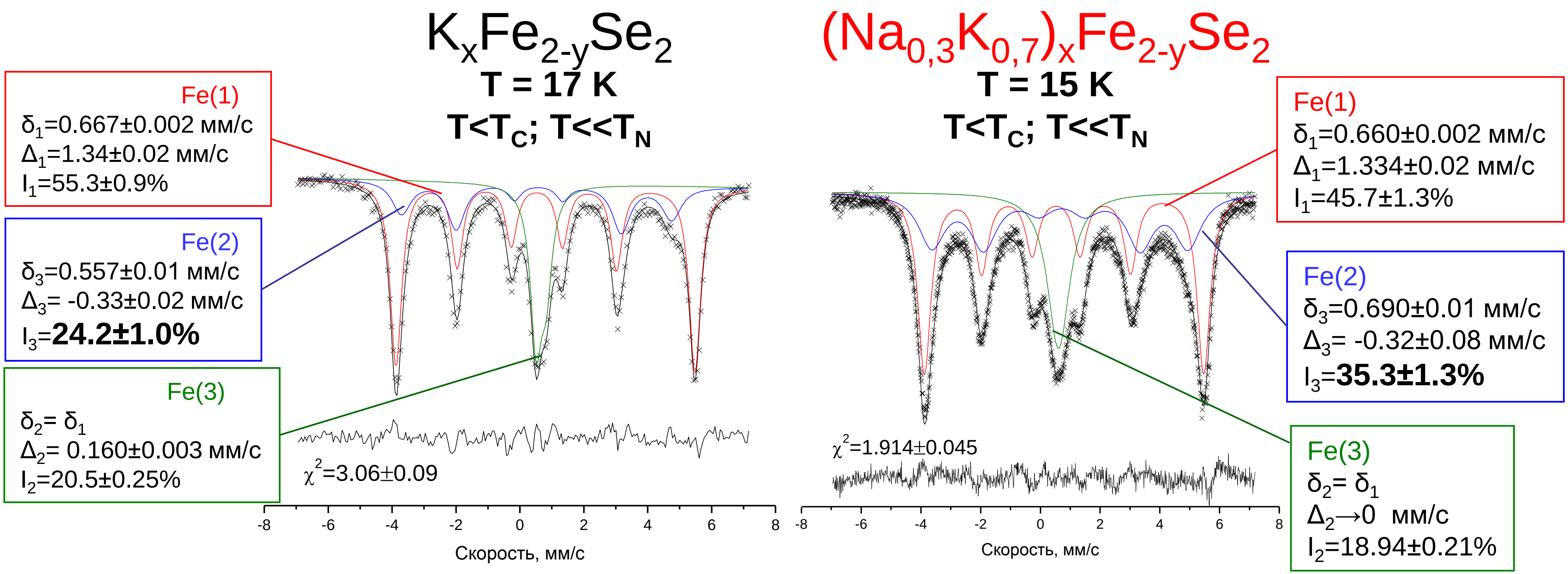
	$A_2Fe_4Se_5$ S.g. I4/m	$A_xFe_2Se_2$ S.g. I4/mmm
A=K	*a* = **8.7031**(2)Å *c* = **14.1588(4)** Å	***a* = 3.8467(3)** Å ***c* = 14.2312**(4) Å
A=K,Na	*a* = **8.6870(3)** Å *c* = **14.1148(5)** Å	*a* = **3.9397(3)** Å *c* = **14.2241(2)** Å

Features:
Poor crystallinity, multiple phases → Significant broadening of the reflections

Sodium doping significantly increases the a parameter of the $A_xFe_2Se_2$ phase whereas the c parameter remains essentially the same.
For the $A_2Fe_4Se_5$ phase the opposite tendency is observed

!The incorporation of Na induces a strong disorder

The ^{57}Fe Mössbauer spectra of $(Na_{0,3}K_{0,7})_xFe_{2-y}Se_2$ and $K_xFe_{2-y}Se_2$ polycrystalline absorbers



- ^{57}Fe Mössbauer spectrum in the temperature range below T_N can be fitted as a superposition of two magnetic sextets Fe1 and Fe2 and one weakly spitted quadrupole doublet Fe3.
- The co-existance of two magnetically ordered phases with magnetic moments on the Fe1 and Fe2 atoms being 2 and 2.2 μ_B/Fe, respectively. It was shown that the magnetic moments of the Fe1 are aligned along the c-axis while the magnetic moments of the Fe2 are lying in the ab-plane.

Conclusions

1. Samples $(Na_zK_{1-z})_xFe_{2-y}Se_2$ with different degree of substitution was synthesized for the first time. The composition and microstructure of the samples were studied by X-ray diffraction and EDX. It is shown that the maximum degree of substitution of potassium for sodium is about 40%.

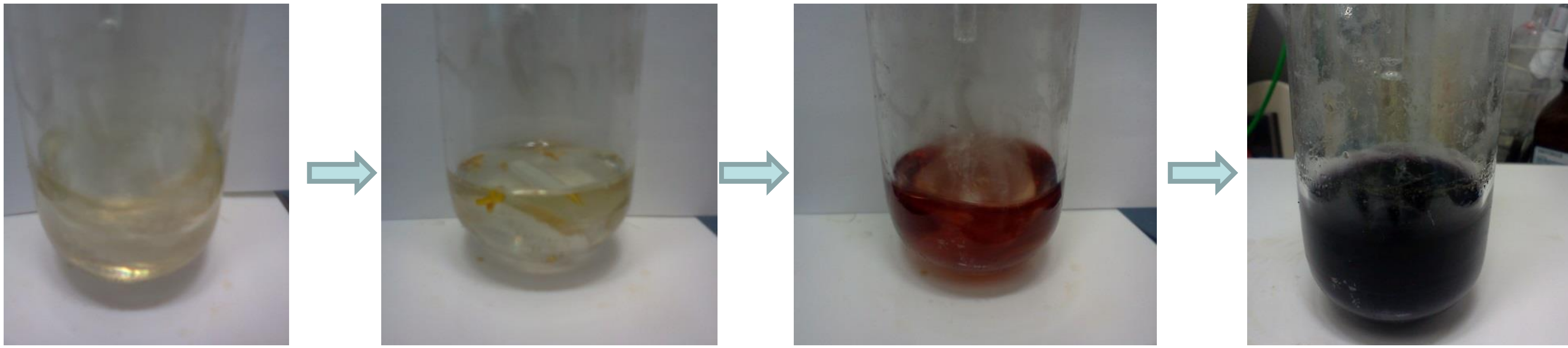
2. The study of magnetic and transport properties showed that the sodium-potassium ferroselenids are superconductors with maximum T_C 32.5 K.

3. The study of the microstructure of the sample $(Na_{0.3}K_{0.7})_xFe_{2-y}Se_2$ by synchrotron radiation and Mössbauer spectroscopy revealed a phase separation of the sample. Mössbauer spectra consist of two magnetic and one paramagnetic components and, when grinding the content of second magnetic component increases from 6% to 35%, while the superconducting fraction decreases sharply.

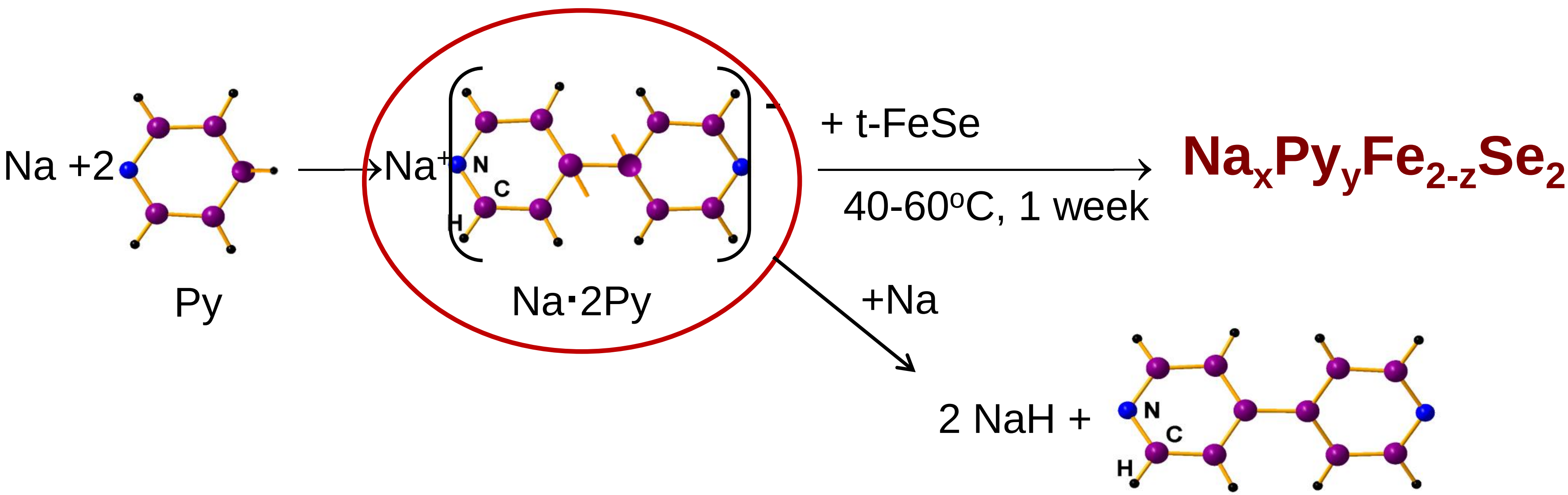
IV. Synthesis of ferroselenids $\boldsymbol{A_x(C_5H_5N)_yFe_{2-z}Se_2}$ **(*A*=Li, Na)** by intercalation of Li and Na to FeSe in pyridine.

Synthesis of samples $A_x(C_5H_5N)_yFe_{2-z}Se_2$ (A=Li, Na) by methods a soft chemistry

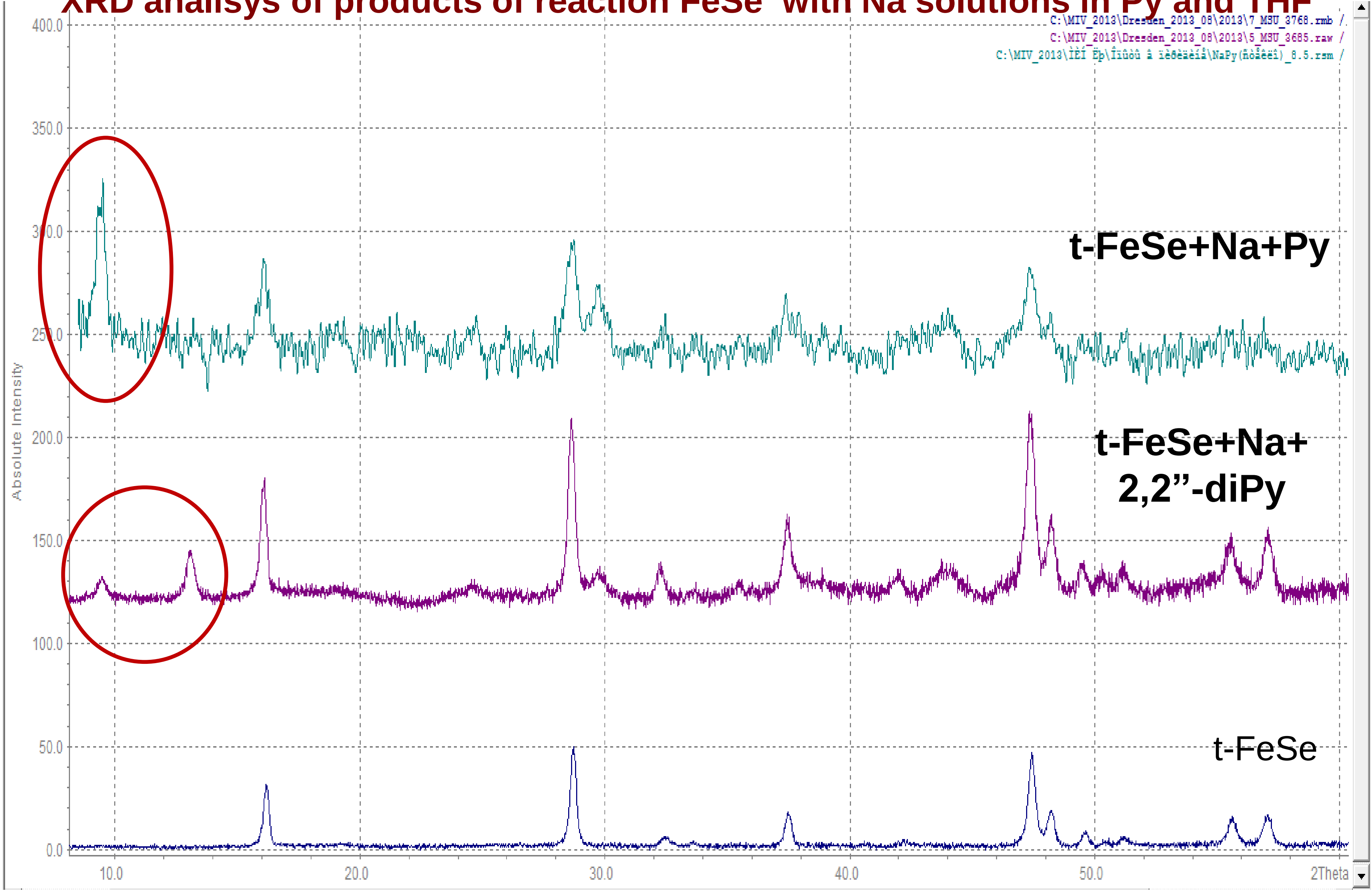
The intercalation of alkali metal in t-FeSe from pyridine solution.



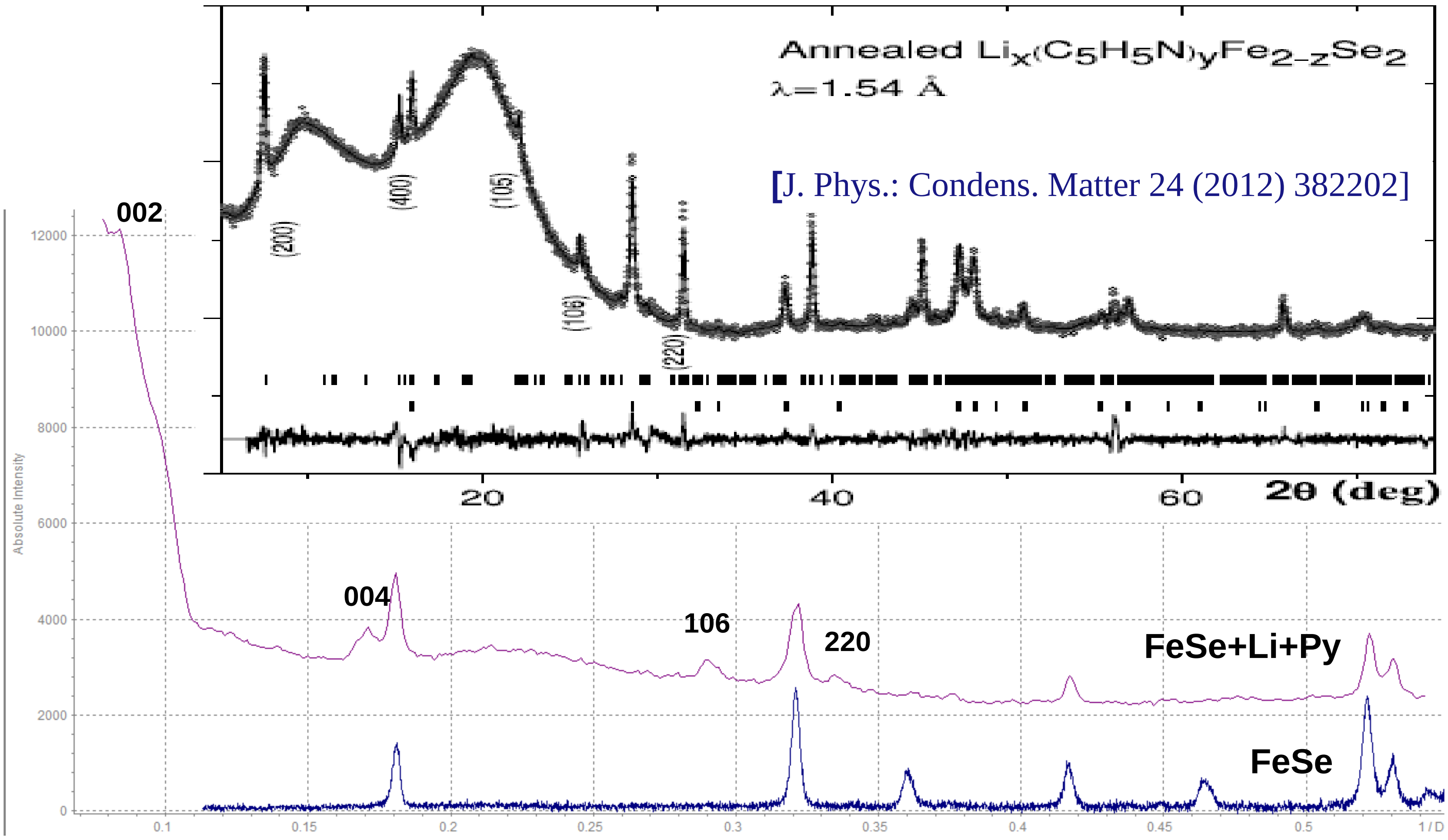
8 min | 10 min | 17 min | 30 min



XRD analisys of products of reaction FeSe with Na solutions in Py and THF

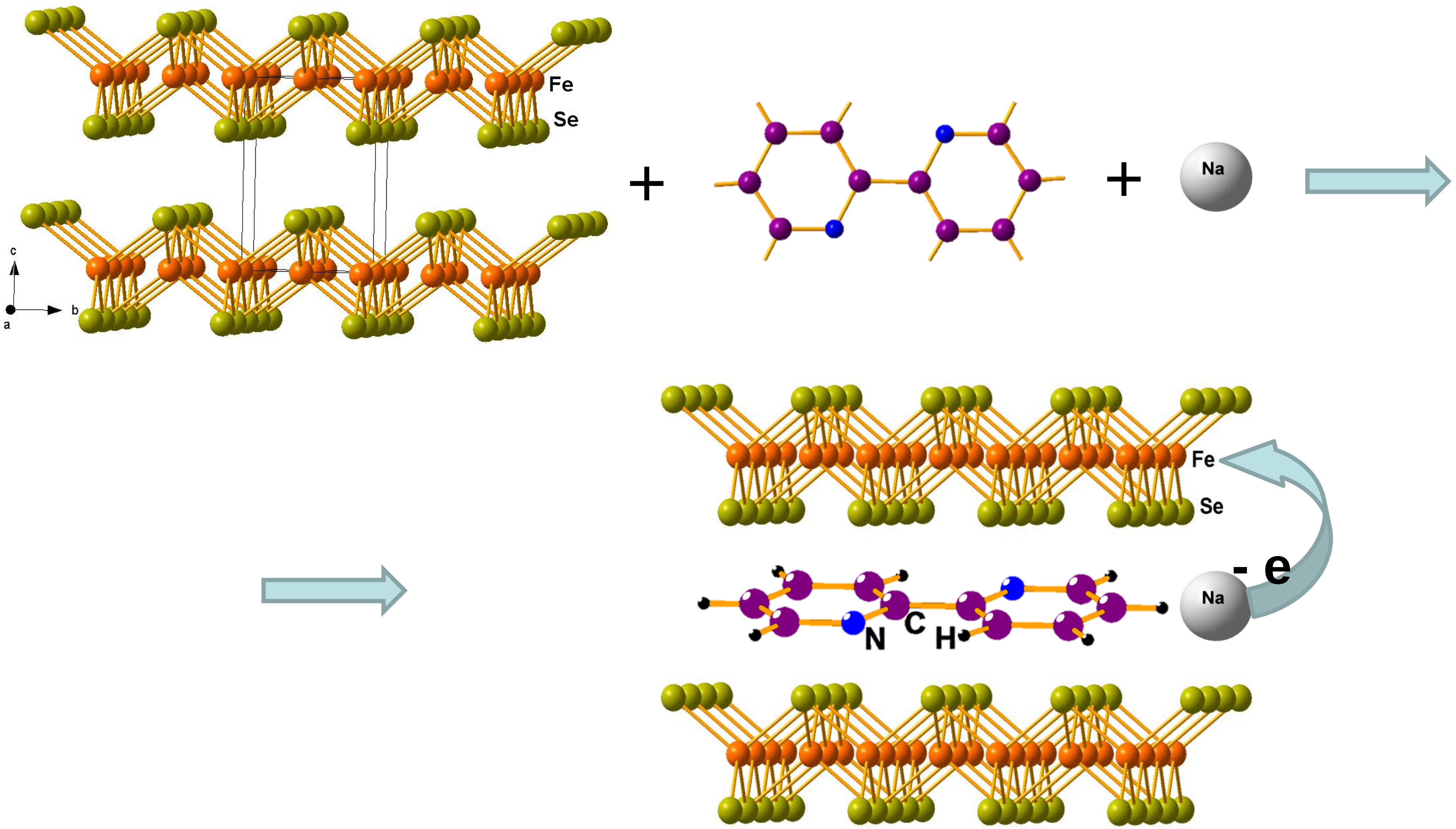


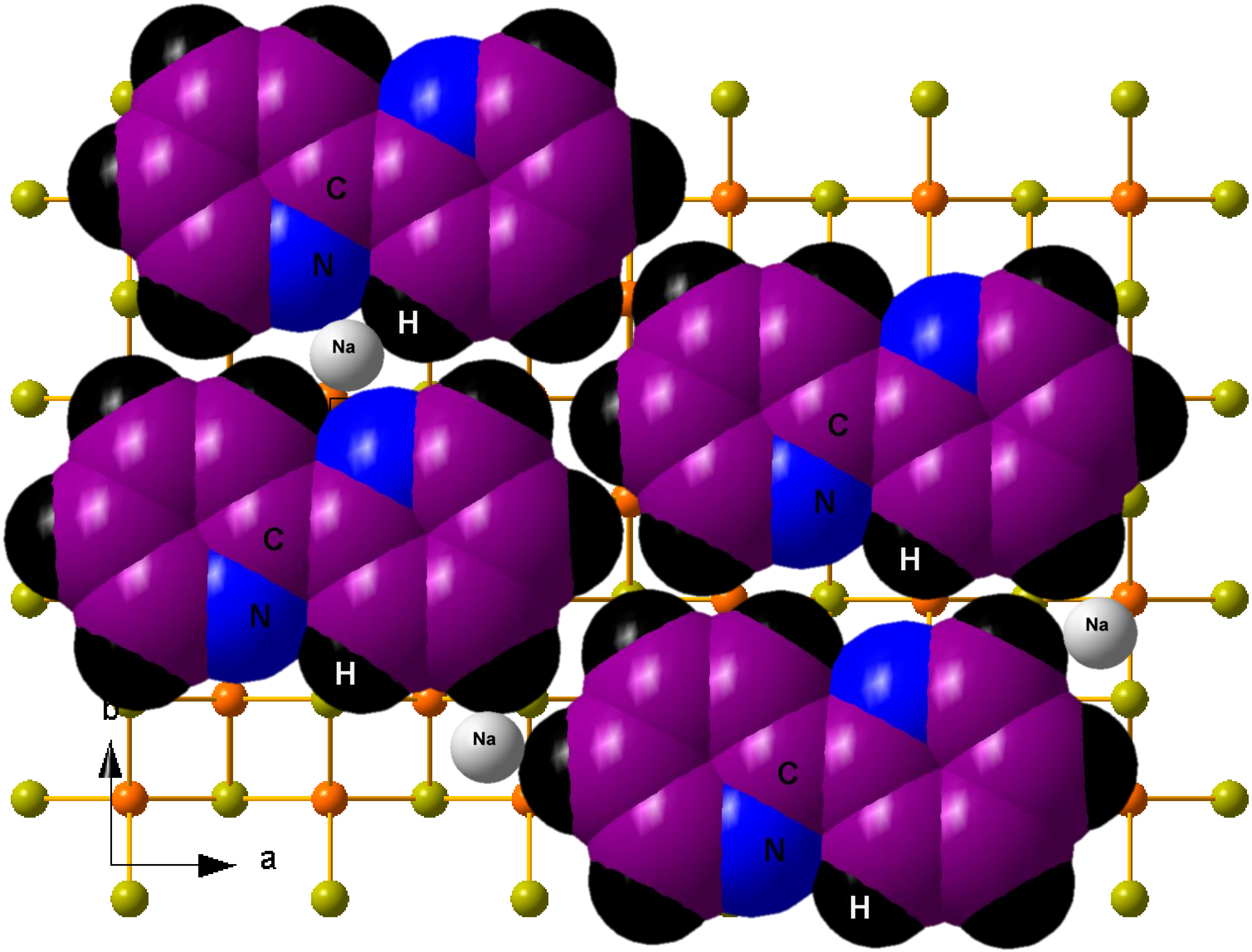
Li + FeSe + Py



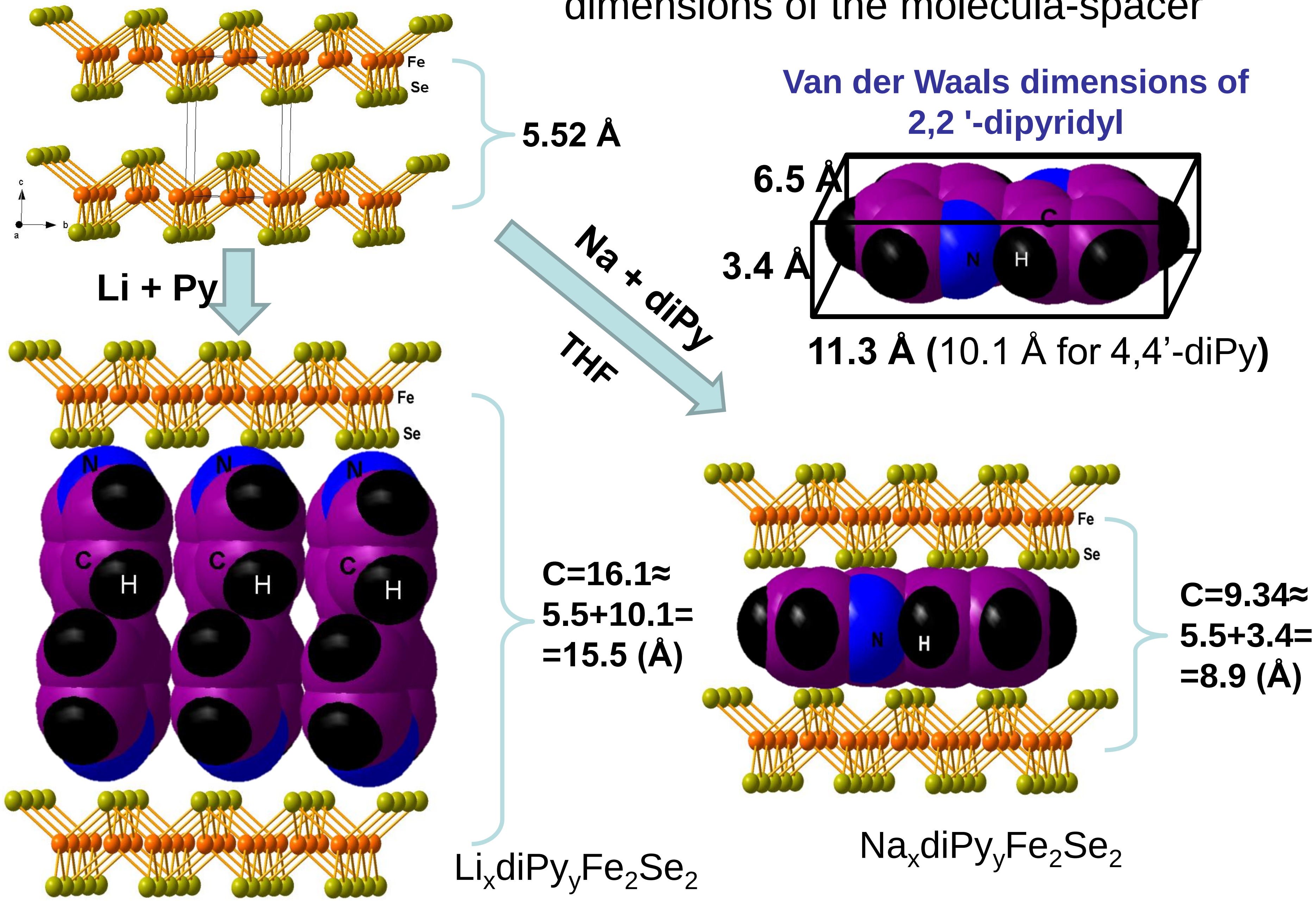
Annealed $Li_x(C_5H_5N)_yFe_{2-z}Se_2$
λ=1.54 Å
[J. Phys.: Condens. Matter 24 (2012) 382202]
(200)
(400)
(105)
(106)
(220)
20
40
60
2θ (deg)
002
004
106
220
FeSe+Li+Py
FeSe
Absolute Intensity
12000
10000
8000
6000
4000
2000
0
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
1 / D

Intercalation of t-FeSe by sodium and 2.2 '- dipyridyl in THF




C
N
H
Na
C
N
H
C
N
H
Na
Na
C
N
H
b
a

The relationship between the interlayer distance and the Van der Waals dimensions of the molecula-spacer



Conclusions

1. Lithium and sodium ferroselenides was prepared by the methods of "soft chemistry" from the solution in pyridine (20-60 ^{o}C) by two ways:
   - by alkali metal intercalation in FeSe;
   - by substitution of potassium in $K_xFe_{2-y}Se_2$ on Na or Li.

2. It is shown that as spacer molecules can act dipyridyl.

Collaborations

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IFW Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden

Aswartham, S., L. Harnagea, Wurmehl S., Büchner B.

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Lebedev O.I.

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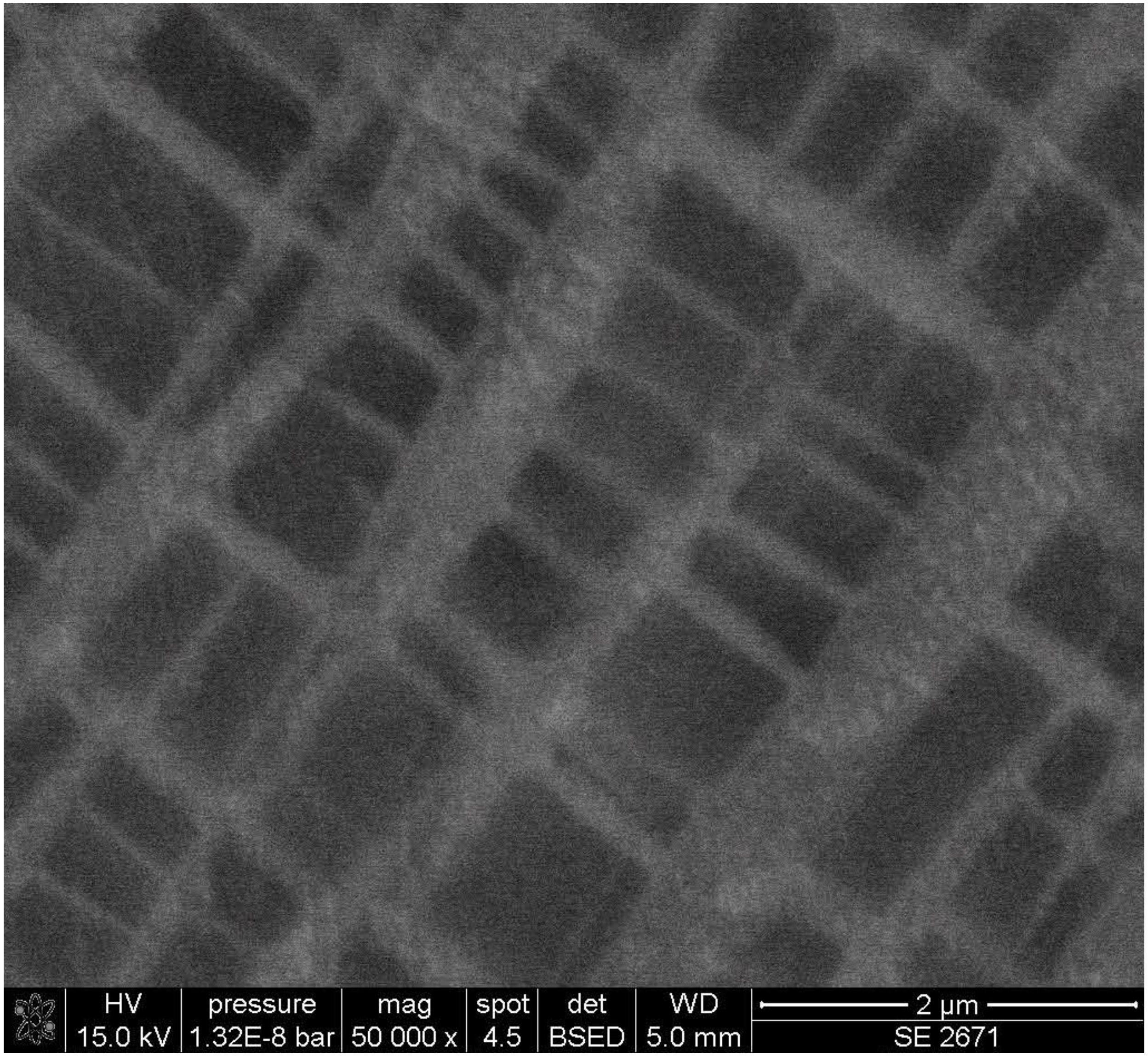
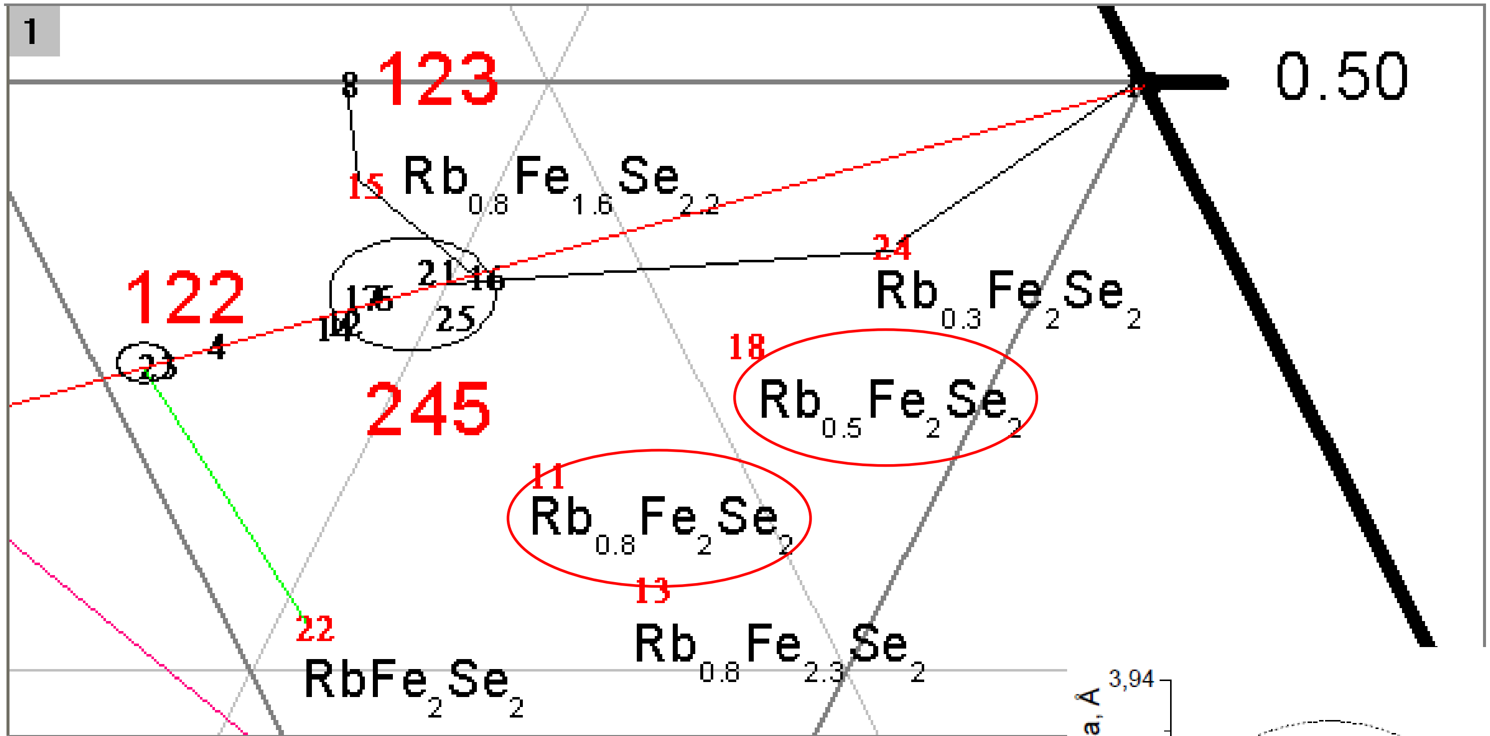
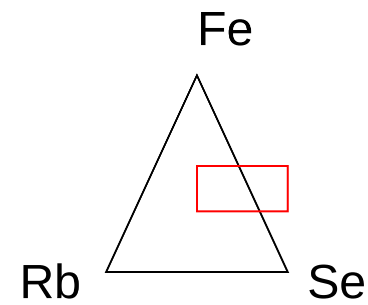
Thank you for attention!

Spinodal decomposition?



Compositional diagram Rb-Fe-Se

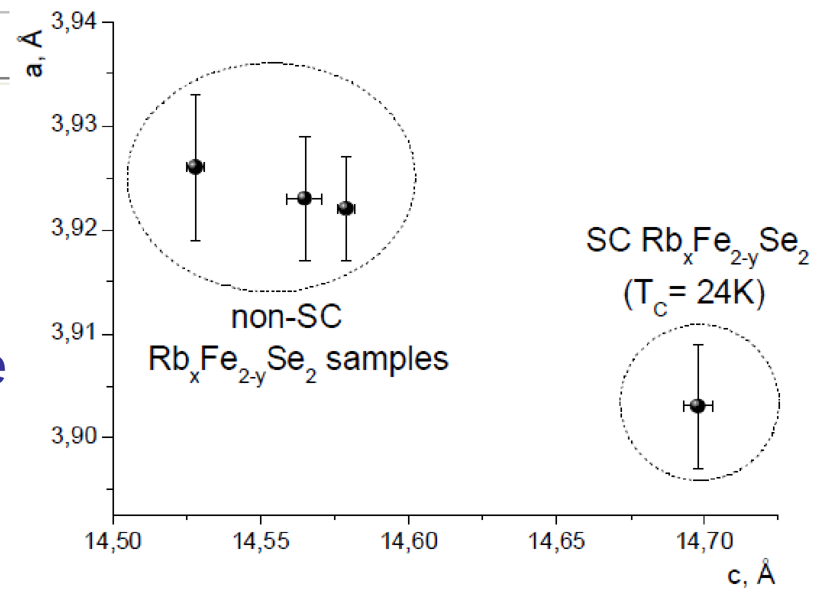




A different ratio Rb-Fe-Se:

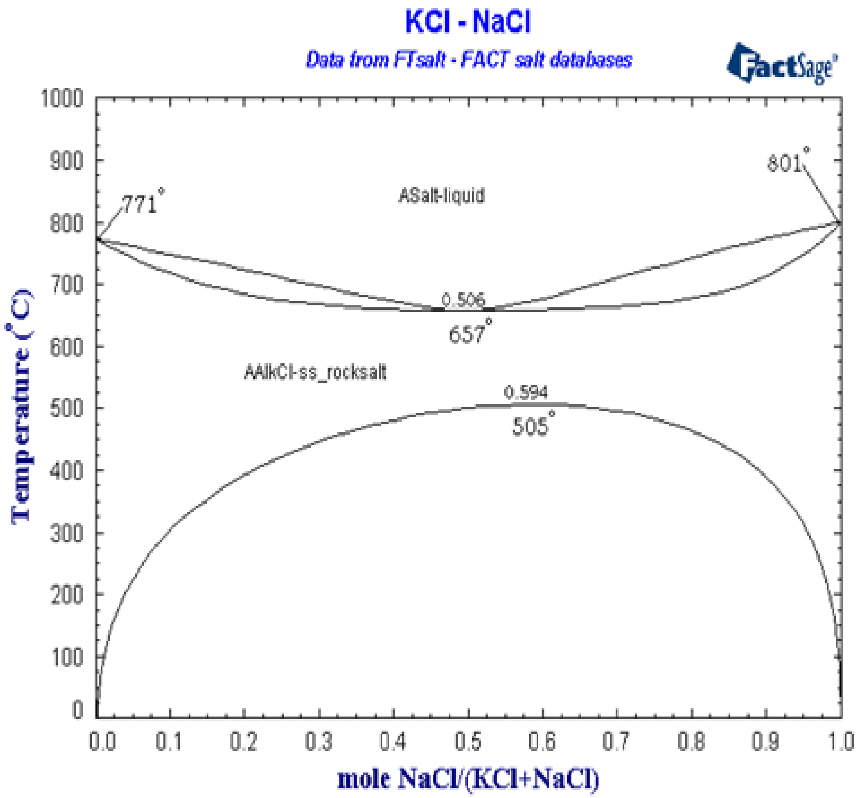
$Rb_{0.8}Fe_2Se_2 = Rb_{0.73(6)}Fe_{1.72(3)}Se_2$

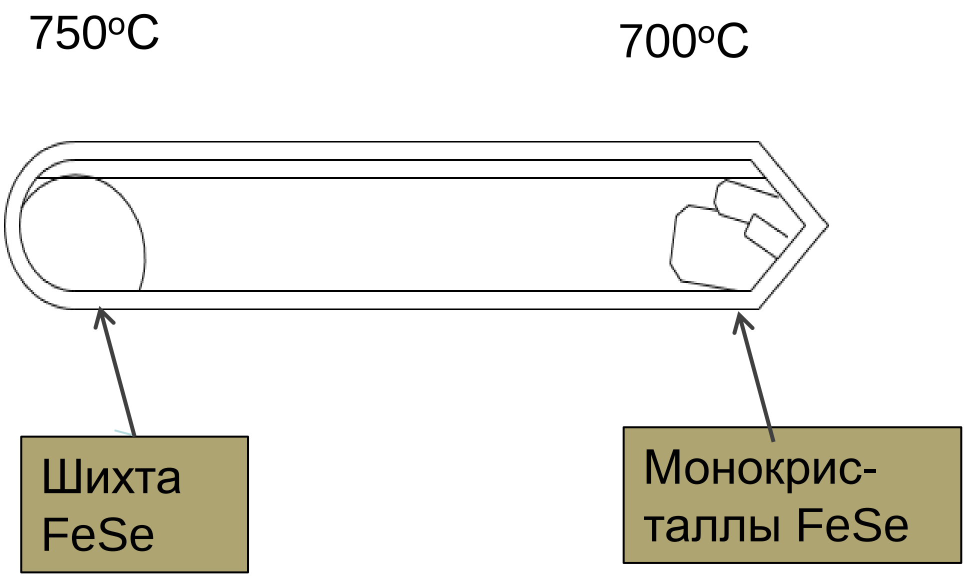
$Rb_{0.5}Fe_2Se_2 = Rb_{0.75(1)}Fe_{1.66(3)}Se_2 + Fe_{1+\delta}Se$



VI. Синтез образцов $(Na_zK_{1-z})_xFe_{1-y}Se_2$ альтернативными методами

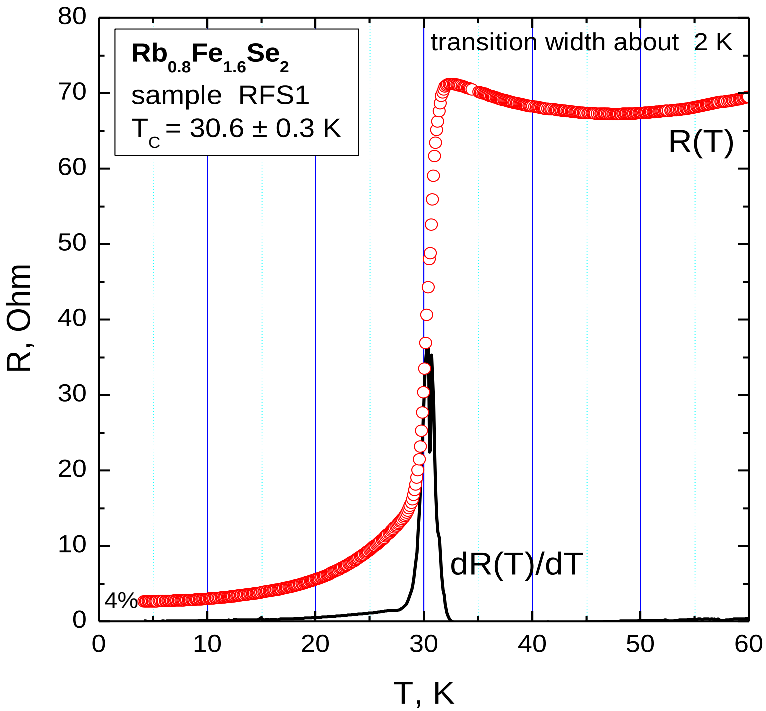
Синтез монокристаллов FeSe в эвтектических расплавах галогенидов щелочных металлов в условии стационарного градиента температур

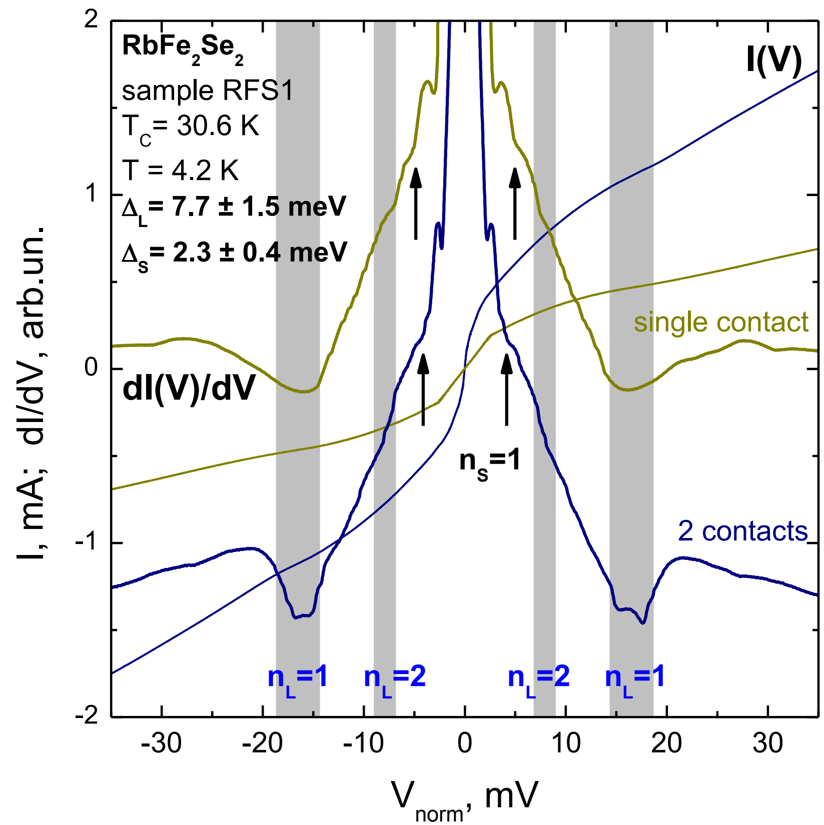




В качестве шихты вместо FeSe загружены образцы $\boldsymbol{A_{0.8}Fe_2Se_2}$, $\boldsymbol{A}$ **= K, Na, Li**

Resistivity measurements and the multiple Andreev reflections effect spectroscopy





The large and the small superconducting gap values were determined at T = 4.2 K: $\boldsymbol{\Delta_L = 7.7 \pm 1.5}$ ***meV***, $\boldsymbol{\Delta_S = 2.3 \pm 0.4}$ ***meV***. The corresponding BCS-ratios were found to be $2\,\Delta_L/kT_C >> 3.52$, and $2\,\Delta_S/kT_C << 3.52$, conclude on a strong electron-boson coupling in the bands with the large gap, and on an induced superconductivity in the bands with the small gap.