Laboratory for Neutron Scattering

Laboratory for Developments and Methods

Swiss-Norwegian Beam Lines at ESRF

ESRF

Paul Scherrer Institut

Symmetry, magnetism and phase coexistence in superconducting iron chalcogenides AyFe2-xSe2 (A=K, Cs, Rb)

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A diffraction view on the crystal structures, antiferromagnetic ordering and intrinsic phase separation in alkali-metal iron chalcogenides.

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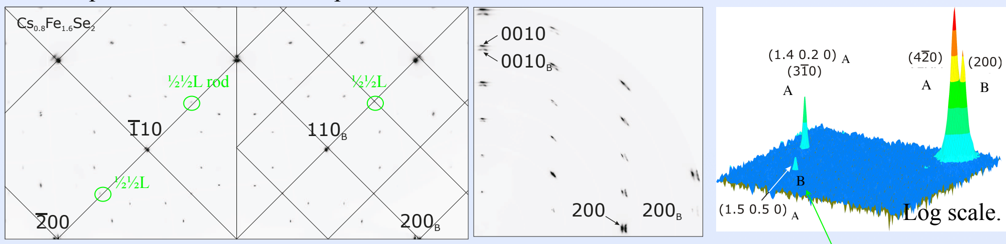
Phase separation as seen by:

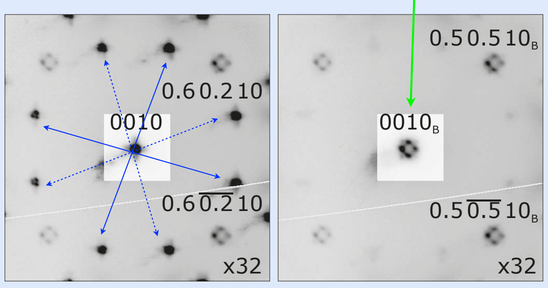
Single crystal synchrotron x-ray

Two metrically different phases: main AFM vacancy ordered (A) and vacancy free (B)

Mesh: phase A   Mesh: phase B

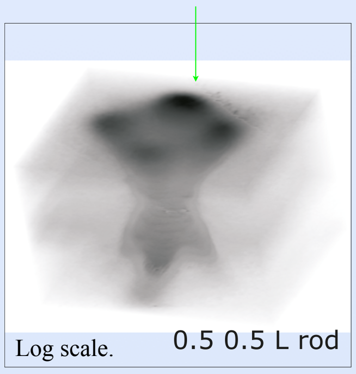


A has two twins in (ab)   B has two four 100-twins

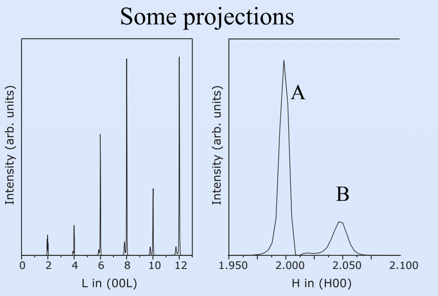


The satellite reflections of phase A are indicated by arrows for the stars $\{k_1\}$={[2/5,1/5,1]} and $\{k_2\}$ ={[1/5,2/5,1]} by solid and dashed lines. The indexing is given in the average cell I4/mmm

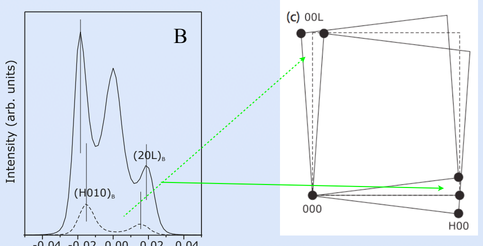
Rods of minority phase B. Log scale. Origin: in plane 2D ordering of alkali-earth. Also 4 twins



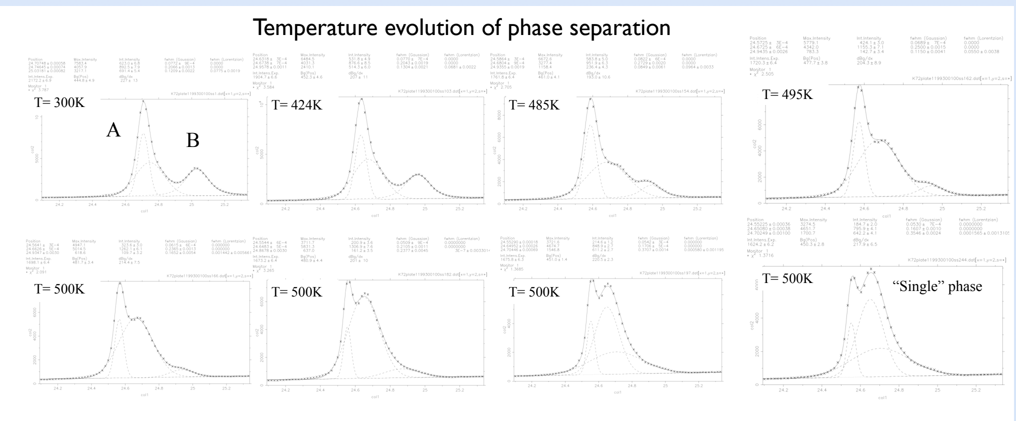
Some projections



B phase rocking curves show small monoclinic distortion.



100-rotational twinning



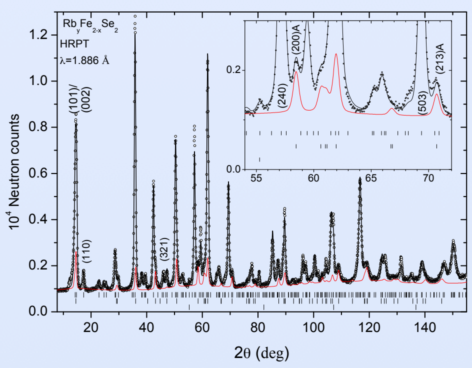
Summary:

The ground state of the crystal is an intrinsically phase-separated state with two distinct-by-symmetry phases. The main phase has the iron vacancy ordered √5×√5 superstructure (I4/m space group) with AFM ordered Fe spins. The minority phase does not have √5×√5-type of ordering and has a smaller in-plane lattice constant a and larger tetragonal c-axis and can be well described by assuming the parent average vacancy disordered structure (I4/mmm space group) with the refined stoichiometry Rb0.60(5)(Fe1.10(5)Se)2. The minority phase amounts to 8–10% mass fraction. The minority phase merges with the main vacancy ordered phase on heating above the phase separation temperature TP = 475 K. The spatial dimensions of the phase domains strongly increase above TP from 1000 to >2500 Å due to the integration of the regions of the main phase that were separated by the second phase at low temperatures.

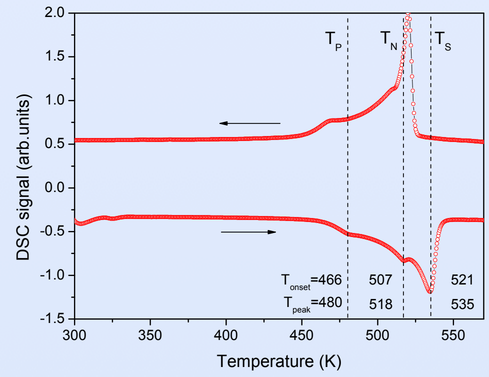
Using the arguments of commensurability and detailed analysis of twinning patterns, we augment the previous findings by quantifying the intergrowth state, consisting of the tetragonal phase with ordered Fe vacancies and the minor disordered phase. Compared to the main phase, the minor one is compressed in the tetragonal *a*-*b* plane and expanded along the *c* direction; a set of modulated Bragg rods evidences a planar disorder. Fourfold splitting of the rods and main Bragg peaks implies a rotational twinning; close inspection of the lattice metric indicates that the symmetry of the minor phase is not higher than monoclinic, with a deviation from the orthogonal basis of ~0.25°.

Powder neutron diffraction

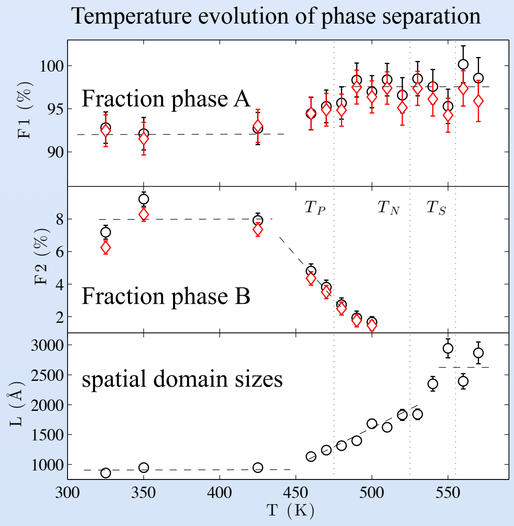
Contribution of the minority in-plane compressed phase B (refined in the average crystal structure I4/mmm) is shown by red curve.



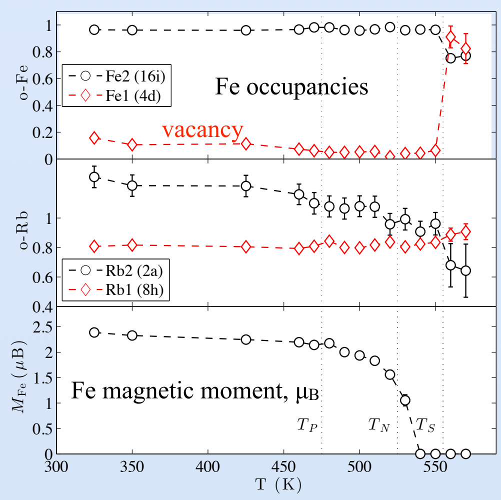
Differential scanning calorimetry (DSC) signal as a function of temperature. Three peaks are observed: the largest at Ts = 535 K corresponds to the structure phase transition due to the vacancy ordering, T_N and T_P are related to AFM ordering and phase separation, respectively.



Temperature evolution of phase separation



phase A

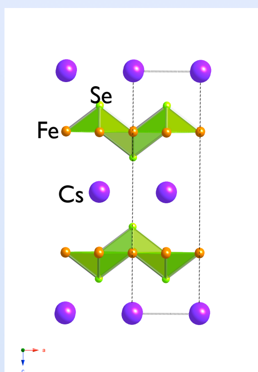


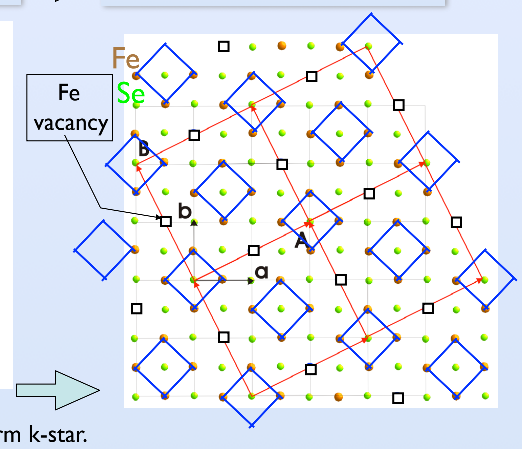
Crystal structure

122 *I4/mmm* average structure $X_yFe_{2-x}Se$

I4/m vacancy ordered√5×√5 structure. Ideal order at x=0.4

Structure transition details





Basis transfomation
$\mathbf{A} = 2\mathbf{a} + \mathbf{b}$
$\mathbf{B} = -\mathbf{a} + 2\mathbf{b}$
$\mathbf{C} = \mathbf{c}$

Position splitting

Cs (2a) (0,0,0) → (2a) (0,0,0); (8h) (x,y,0)

Fe (4d) (0, ½, ¼) → "vacancy" (4d) (½,0,¼); (16i) (x,y,z)

Se (4e) (0,0,z) → (4e) (½, ½,z); (16i) (x,y,z)

For ideal vacancy order $Cs_2Fe_4Se_5 = Cs_{0.8}Fe_{1.6}Se_2$

really: $A_yFe_xSe_2$

y=0.7-0.85, x=1.60-1.75

I4/mmm->I4/m with 4 arm k-star.

10 independent distortion modes: 2 order + 8 displacive