Spectromicroscopy of phase-separated iron-chalcogenide superconductors

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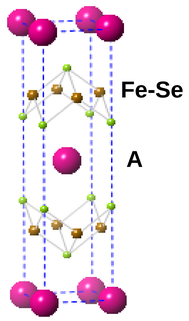
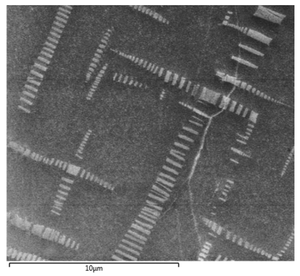
Introduction

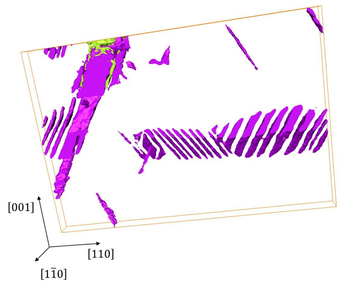
Understanding the interplay between magnetic order and superconductivity in iron-based superconductors is likely to provide important insights into the elusive mechanisms responsible for high temperature superconductivity. In single crystals of alkali metal doped iron selenide, $A_xFe_{2-y}Se_2$ (A=K, Cs, Rb), a superconducting phase with $T_c \approx 30K$ coexists with an antiferromagnetic phase with $T_N \approx 500K$. The intrinsic phase separation is very extreme, with significant chemical and structural differences associated with the spatially distinct electronic phases. Here, a range of complementary electron microscopy and synchrotron-based microscopy techniques have been used to investigate how the fundamental properties of each phase is related to its chemistry and structure.



Morphology

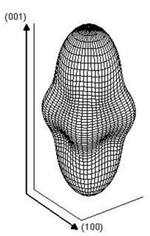
The morphology of the two-phase microstructure has been examined by Scanning Electron Microscopy (SEM) on freshly cleaved (001) surfaces and cross-sections prepared in-situ by focussed ion beam (FIB) milling to show the presence of a crystallographically-aligned network of plate-shaped minority phase with {113} facets.



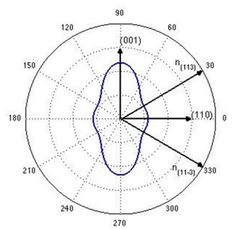


Avizo 3D reconstruction of minority phase from serial FIB sectioning of a $Rb_xFe_{2-y}Se_2$ single crystal.

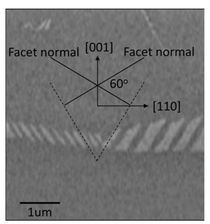
The energy surface of the minority phase has been calculated from the stress-free transformation strain [1] using the elastic constants calculated by DFT by Ivanovskii [2] and the lattice parameters of the two phases measured by XRD [3]. The minimum in the energy surface is found to correspond to the observed facet angles.



Energy surface



Projection of energy surface on $(1\bar{1}0)$ plane.

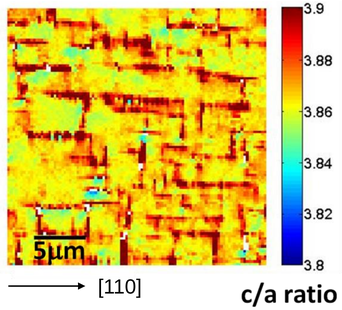


FIB cut of $(1\bar{1}0)$ plane.

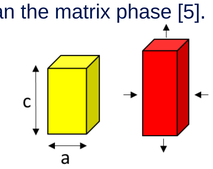
References [1] Speller et al PRB 90 024520 (2014), [2] Ivanovskii et al Phys. C 471 409 (2011); [3] Pomjakushin et al J Phys. Condens. Matter 24 435701 (2012); [4] Speller et al APL 99 192504 (2011); [5] Speller et al SUST 25 084023 (2012); [6] Mou et al Frontiers of Phys. 6 410 (2011); [7] Speller et al J Novel Supercond. Mater. 1 30 (2015); [8] Ricci et al PRB 91 020503R (2015;.

Acknowledgements
Prof Asensio and Dr Avila, Antares beamline, Soleil Synchrotron; Dr Maccherozzi, I06, DLS.

Crystal structure

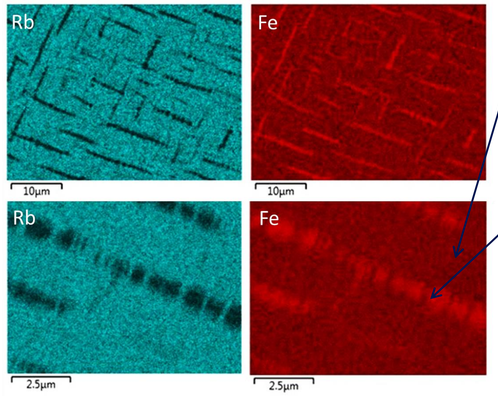


The high resolution electron backscatter diffraction (EBSD) technique, described in [4], has been performed on cleaved (001) surfaces to map the unit cell (c/a) ratio. The minority phase in $Cs_xFe_{2-y}Se_2$ (shown) and $Rb_xFe_{2-y}Se_2$ crystals have more anisotropic unit cells than the matrix phase [5].



Chemical composition

High spatial resolution energy dispersive x-ray (EDX) microanalysis using a SEM at low accelerating voltage (5kV) and a large area Oxford Instruments X-max detector.

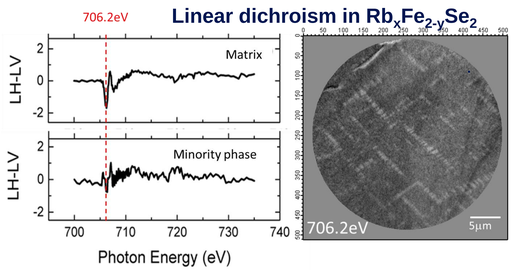


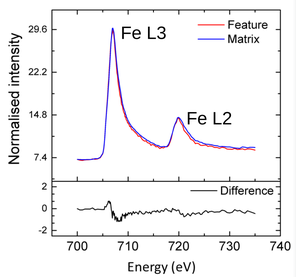
Matrix phase
- $Rb_{0.8}Fe_{1.6}Se_2$
- Likely to be Fe-vacancy-ordered phase known to be AFM and insulating [6].
- Fe deficiency enables Fe to be in 2^+ valence state.

Minority phase
- Composition difficult to measure accurately owing to sub-micron sized features.
- Richer in Fe – close to vacancy-free composition.
- Lower Rb content.

Magnetic properties

Photoelectron emission microscopy (PEEM) using synchrotron X-rays at Diamond Light Source. Fe X-ray absorption spectra (XAS) have been reconstructed from the matrix and minority phases.
X-ray linear dichroism (XLD) images and spectra are produced from the difference in intensity of photoelectrons using horizontally-polarised (LH) and vertically-polarised (LV) incident x-rays [7].





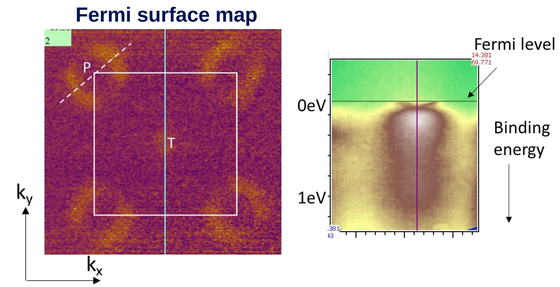
Matrix phase
- Signature of AFM ordering in XLD spectrum.

Minority phase
- No AFM ordering seen in spectrum.

Electronic structure

Angle-resolved photoemission spectroscopy (ARPES) is a very surface sensitive technique for measuring the electronic structure of crystals.

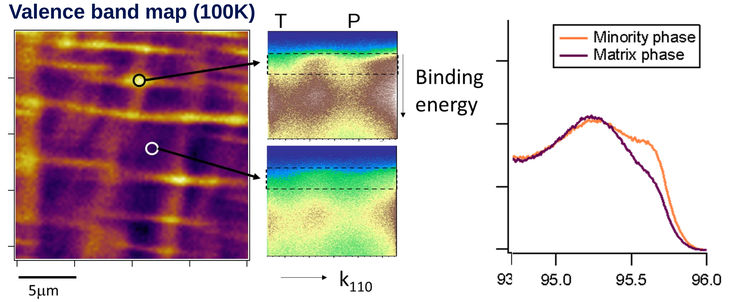
Fermi surface map



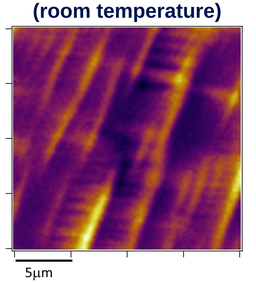
High resolution (~2meV) ARPES at Diamond Light Source shows that there are electron pockets at the T and P points of the Fermi surface in $Rb_xFe_{2-y}Se_2$.
The dispersion of the electron pockets at the P point is clearly resolved in the high symmetry cut shown.

Classical ARPES (above) uses a spot size of about 100μm, obtaining average data from both phases. To investigate the electronic structure of each phase separately, the incident light is focussed into a sub-micron spot and scanned across the sample. This reduces the intensity and energy resolution.

Valence band map (100K)



Valence band map (room temperature)



NanoARPES on the Antares beamline at the Soleil synchrotron shows the electron dispersion in each phase. Spectra integrated over momentum reveal the minority phase has a significantly higher occupied density of states just below the Fermi level originating from the Fe 3d bands.

Matrix phase – insulating
Minority phase – metallic/superconducting

The minority phase appears more continuous in VB maps taken at 100K than at room temperature. VB maps at room temperature have a more discontinuous appearance suggesting an electronic phase transition may occur between room temperature and 100K as reported by Ricci et al [8].

Conclusions

- **Matrix phase** is insulating and antiferromagnetic with a Fe-deficient chemical composition close to the known Fe-vacancy-ordered $A_2Fe_4Se_5$ phase.
- **Minority phase** is metallic at 100K and likely to become superconducting at low temperature. It is non-magnetic and has a higher Fe content.