SAPIENZA UNIVERSITY OF ROME
PHYSICS DEPARTMENT

PHD IN MATERIAL SCIENCE

STRUCTURAL TRANSITION AND PHASE SEPARATION STUDIES FOR SUPERCONDUCTING MATERIAL DESIGNING

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PHD CICLE XXIV (2008-2011)
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Ph.D. in Material Science
Thesis Title: "Structural transition and phase separation studies for Superconducting material designing"
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Introduction

The recent discovery of high-temperature superconductivity (HTS) in the iron pnictides [1] has provided a new class of materials for the search of the physical mechanism that allows a quantum coherent condensate to avoid the effects of temperature decoherence. The discovery of HTS in LaO$_{1-x}$FeAsF$_x$ was soon followed by the discovery of a different class of superconducting iron-based compounds, among which the quaternary systems “1111” (REFeAsO, RE stands for rare earth) and ternary ”122” (AFe$_2$As$_2$, A stands for Ba, Ca, Sr, etc.) systems are the most investigated. Superconductivity arises in the 1111 systems by the partial fluorine substitution for the oxygen, or by the creation oxygen defects. On the other hand, substitution of Fe by K, Ni, etc. is found to result in the superconducting transition in the 122 systems. Interestingly, in both cases, the bulk superconductivity appears by the suppression of the long-range magnetic ordering of the parent compounds. The parent compounds, which do not show superconductivity (SC), show a structural transition from the room temperature tetragonal to the low temperature orthorhombic structure. In the 1111 systems, the structural and magnetic transitions do not coincide, whereas the structural and magnetic transitions coincide in the 122 systems.

The tetragonal-to-orthorhombic structural phase transition (SPT) in LaFeAsO (La-1111) and SmFeAsO (Sm-1111) single crystals measured by high-resolution x-ray diffraction is found to be sharp while the RFeAsO (R=La, Nd, Pr, Sm) polycrystalline samples show a broad continuous SPT. Comparing the polycrystalline and the single-crystal 1111 samples, the critical exponents of the SPT are found to be the same while the correlation length critical exponents are found to be very different. These results imply that the lattice fluctuations in 1111 systems change in samples with different
surface to volume ratio that is assigned to the relieve of the temperature-dependent superlattice misfit strain between active iron layers and the spacer layers in 1111 systems. This phenomenon that is missing in the AFe$_2$As$_2$ (A=Ca, Sr, Ba) “122” systems, with the same electronic structure but different for the thickness and the elastic constant of the spacer layers, is related with the different maximum superconducting transition temperature in the 1111 (55 K) versus 122 (35 K) systems and implies the surface reconstruction in 1111 single crystals. Superconductivity has been induced by oxygen defects in the fluorite spacers in iron-based oxypnictides Sm[O$_{1-x}$]FeAs, Nd[O$_{1-x}$]FeAs and Pr[O$_{1-x}$]FeAs with the maximum critical temperature being 43, 51.9 and 52 K, respectively. Oxygen defects induce electron doping of the Fe derived bands crossing the Fermi level and the electronic/magnetic structure is very sensitive to different atomic substitutions and rare-earth (RE) ions. The change of the RE atomic radius induces a change of the elastic misfit strain between the superconducting Fe layers and the intercalated layers, like in cuprates, and diborides.

Superconductivity, with transition temperature, $T_c$, above 30 K, has been reported also in a new discovered family of Fe-based high temperature superconductors (HTS) A$_x$Fe$_{2-y}$Se$_2$. These systems are made of iron chalcogenide FeSe molecular layers, intercalated by A=K,Cs,Rb,Tl, (Tl,Rb), (Tl,K) spacer layers, providing the more recent practical realization of metal heterostructures at atomic limit, as cuprates and pnictides high temperature superconductors. These A$_x$Fe$_{2-y}$Se$_2$ chalcogenide superconductors show both high temperature superconductivity and magnetism. In these compounds, one may tune the interplay of superconductivity and magnetism by changing the Fe-vacancy order and the superlattice misfit strain. The open question answered in this thesis is whether there is a co-existence of magnetism and superconductivity in the same spatial region or these phenomena occur in different spatial regions dictated by the phase separation. In order to understand the complex behaviour of superconductors and to answer this key question, advanced synchrotron radiation focusing down to a size of 300 nm has been used to visualize nanoscale phase separation in the K$_{0.8}$Fe$_{1.6}$Se$_2$ superconducting system using scanning nano-focus single crystal X-ray diffraction. The results show an intrinsic phase separation in K$_{0.8}$Fe$_{1.6}$Se$_2$ single crystals at T< 520 K, revealing coesistance of; i) a magnetic phase characterized by an ex-
expanded lattice with superstructures due to Fe vacancy ordering and; ii) a non-magnetic phase with an in-plane compressed lattice. The spatial distribution of the two phases at 300 K shows a frustrated or arrested nature of the phase separation. The space resolved imaging of the phase separation permitted us to provide a direct evidence of nano phase domains smaller than 300 nm and different micron size regions with percolating magnetic or non-magnetic domains forming a multiscale complex network of the two phases. The phase separation appears on multiple scales from micron-scale to nano-scale in cuprates, diborides and pnictides. Several theories have described the complex phase separation as an intrinsic feature of all known HTS.

The multilayer architecture, a common feature of cuprates, diborides, pnictides and chalcogenides, underlines the relevance of lattice effects for high-temperature superconductivity. The structure of the iron pnictide superconductors is made of a superlattice of $[\text{FeAs}]_n^{Q+\delta}$ with $Q = 1$, layers intercalated by spacers (oxide layers like $[\text{LnF}_y\text{O}_{1-y}]_n^{Q-\delta}$ or $[\text{LnFO}_{1-y}]_n^{Q-\delta}$ in the “1111” family or metallic atomic layers $[(\text{A}^{2+}_1\text{B}^{1+}_x)_{1/2}]_n^{Q-\delta}$ in the “122” family, and therefore they represent practical realizations of a ‘heterostructure at the atomic limit’ (HsAL) that was described to be the essential material architecture for the emergence of HTS. All of them contain a characteristic layer of FeAs layers made of a tetrahedral network (with As atoms located at the apical sites of the tetrahedron) corresponding to the featured planar $\text{CuO}_2$ plane in cuprates and honey-comb 2D lattice of boron in diborides. In pnictides and chalcogenides, EXAFS and XANES measurements have shown the local lattice fluctuations like in cuprates. These results have recently been applied to design a new heterostructure at the atomic limit for functional materials. In fact, at the end of this thesis we propose a novel class of heterostructures made of alternate layers of pnictides and cuprates to produce an High-Temperature multiband Superconductor (HTMS) material which have additional microscopic degrees of freedom. These HTMS are multilayers involving alternate layer components from cuprate and iron-arsenide superconductor families. In particular, we provide a specific example of a composite system involving two basic components, $\text{Nd}_2\text{CuO}_4$ and $\text{NdOFeAs}$. The idea of such a HTMS is motivated by the striking similarities in the structural and electronic (as evidenced by the Nd $L_3$-XANES) properties of the $\text{Nd}_2\text{CuO}_4$ and $\text{NdOFeAs}$ systems. The electronic
properties and the XANES calculations for this novel HTMS are presented to highlight the importance of such a superstructure which offers further scope for the material manipulation and design of high temperature superconductors.
Chapter 1

The discovery of Iron-based Superconductors

1.1 The Fe-pnictides Superconductors

The discovery of superconductivity in a compound containing iron: $LaFeAsO_{1-x}F_x$ reported by Kamihara et al. on 23rd February 2008 has newly enhanced the attention of researchers in condensed-matter physics and in particular in superconductivity. This compound showed superconductivity at a relatively high temperature of 26 K in $LaFeAsO_{0.89}F_{0.11}$. Therefore, the increasing of superconductive critical temperature up to 40K has been shown by Takahashi et al. studying the same material under a high pressure of $\approx 4$ GPa. After the discovery of the first iron-pnictides researchers reported that with the substitution of rare-earth atoms the $T_c$ of these systems jumps up to 50 K, which is the highest from the discovery of high-$T_c$ cuprates. A lot of researchers have renewed their interest in superconducting field and there are now a very active community that study Fe-based superconductors. The situation after February 2008 is very similar to that when the cuprate superconductor was discovered. Thanks to such competitive research activities, new iron-pnictides superconductors with different crystal structures such as $(Ba,K)Fe_2As_2$ and $LiFeAs$. have been discovered in the last three years. All the families of iron-pnictide superconductors include a two-dimensional (2-D) $FePn$ (Pn: pnictogen atom) layer with a tetragonal structure at room temperature.
Therefore, similarly to those of cuprate, ruthenate and cobaltate superconductors, their physical properties are considered to be highly two-dimensional.[2]

**The 1111-pnictides** These are the iron pnictides of composition RFeAsO, where R is a rare earth (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy), either non-magnetic (La) or magnetic (Ce). The structure of these materials is the ZrCuSiAs type structure (space group P4=nnm), which is shown in Figure 1.1 for the case of NdOFeAs. This family of iron-based superconductors is called the 1111-compounds. It has been reported that approximately 300 RTPnO compounds (R: rare earth, T: late-transition metal, and Pn: pnictogen) belong to this type of structure to date. The RO and FeAs layers are stacked
along the c-axis. The first discovered iron-pnictide superconductor $\text{LaFeAsO}_{1-x}F_x$ has this structure. Undoped RFeAsO is non-superconducting and shows an antiferromagnetic transition at approximately 150 K that change as a function of rare-earth size. At lower temperatures, further magnetic anomalies originating from rare-earth moments, has been observed in some compounds. It is possible to transform the 1111-pnictides from non-superconductive to superconductive replacing $\approx 3\%$ of the oxygen by Fluorine: $\text{RFeAsO}_{1-x}F_x$, or when oxygen deficiency is introduced: $\text{RFeAsO}_{1-\delta}$. After superconductivity appears, $T_c$ is almost constant up to $x = 0.15$. This $T_c$ behavior has been observed in other $\text{RFeAsO}_{1-x}F_x$ systems. The superconductive critical temperature is a function of rare-earth size and change from 25K of $\text{LaFeAsO}_{0.89F_{0.11}}$ to 55K of $\text{SmFeAsO}_{0.9F_{0.1}}$. In 2010 superconductivity has also been observed in the 1111-pnictides $\text{AFe}_{1-x}\text{Co}_x\text{AsF}$ ($\text{A} = \text{Ca and Sr}$) with electron doping. For this family the maximum reachable $T_c$ is 22 K that has been measured in $\text{CaFe}_{0.9}\text{Co}_{0.1}\text{AsF}$ system.

The 122-pnictides This the second discovered iron-pnictide family is characterized by a $\text{ThCr}_2\text{Si}_2$- type structure, as is shown in Figure 1.2. Follow their stechiometry these compounds are called 122-pnictides. The $(\text{R}_2\text{O}_2)^{2+}$ layer in RFeAsO is replaced by a single divalent ion ($\text{A}^{2+}$) layer, and thus the electron count is not altered. With hole doping also $\text{AFe}_2\text{As}_2$ becomes superconducting, it has been achieved through the partial substitution of the A site with monovalent $B^+$: $\text{A}_{1-x}\text{B}_x\text{Fe}_2\text{As}_2$ with $\text{A} = \text{Ba, Sr, Ca, and B = K, Cs, Na}$. Superconductivity also emerges by electron doping via partial substitution of cobalt for iron: $\text{A(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$. The undoped parent 122-pnictides show a similar antiferromagnetic ordering as the 1111-compounds. In the phase diagrams of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, the coexistence of antiferromagnetic ordering with superconductivity was observed but $\mu$SR measurements clarified the phase separation into the superconducting and magnetic phases in 1111 and 122 compounds. Using hydrostatic pressure it is possible to induce superconductivity as well as by partial substitution. From the resistivity measurements of $\text{SrFe}_2\text{As}_2$ under pressure, Kote-gawa et al. reported that superconductivity with a sharp resistive transition appears, accompanied by the suppression of the antiferromagnetic state.
Figure 1.2: Crystallographic structure of the first discovered 122-pnictide: $\text{BaFe}_2\text{As}_2$ (by Ref. [22])
1.2 The Fe-chalcogenides Superconductors

In July 2008 Hsu et al. reported superconductivity at 8 K in anti-PbO-type FeSe. As well as iron-pnictides also Fe-chalcogenides show a high $\mu_0H_{c2}$. FeSe is a very simple heterostructure composed of only FeSe layers with an anti-PbO-type structure (space group: P4/nmm) as is shown in Figure 1.3. For this reason they are called also 11-chalcogenides. The crystal structure of FeSe is the simplest among Fe-based superconductors. Furthermore, a theoretical study indicated the similarity in the electronic states between Fe chalcogenides (FeS, FeSe, and FeTe) and the FeAs-based superconductors. In fact the morphology of the Fermi surface and the contributions of Fe-3d electrons near the Fermi level $E_F$ have some similarities to the FeAs-based. These common features to the FeAs-pnictides have made Fe-chalcogenides a very important and simple system for the understanding of superconductive mechanism in Fe-based superconductors. [3]

Fe-chalcogenides form several types of crystal structures, depending on the elemental composition, synthesis process and synthesis conditions of temperature or pressure. To date, three anti-PbO-type compounds, FeS, FeSe, and FeTe, have been
Chapter 1. The discovery of Iron-based Superconductors

confirmed. Among them, FeTe is the most stable phase, and the single phase can easily be obtained using a conventional solid-state reaction method. With decreasing ionic radius of chalcogen, the PbO structure tends to be unstable. Although FeSe forms with the solid-state reaction, a sample synthesized at high temperatures contains the NiAs-type (hexagonal) FeSe phase. To obtain a single phase of PbO-type FeSe, low temperature annealing around 300-400 °C, which transforms the NiAs-type phase to the PbO-type phase, is required.

The highest \( T_c \) of 11-chalcogenides appears in optimally doped \( FeTe_{1-x}Se_x \), which has the tetragonal structure down to low temperatures. While a higher \( T_c \) appears in the tetragonal phase, the orthorhombic phase of \( FeTe_{1-x}Se_x \) \((0.5 \leq x \leq 1)\) can be superconducting as well. However, superconductivity is not observed in monoclinic phase of FeTe, because the long-range antiferromagnetic ordering appears. These results suggest that the higher \( T_c \) appears in the tetragonal phase close to magnetically ordered FeTe. The magnetic fluctuation play a key role for the understanding of the variation of \( T_c \) in this system.

Although FeSe and FeTe have a similar crystal structure, their physical properties are much different. FeSe has a metallic behavior and undergoes a superconducting transition at \( T_{c\text{onset}} = 13K \). At the contrary, FeTe not show superconductivity an it is characterized by an antiferromagnetic ordering around 70 K where the anomaly appears in the resistivity–temperature curve. Above 4.2 K no magnetic ordering was observed in superconducting FeSe . In contrast, FeTe shows an antiferromagnetic ordering below 70 K. The comparably low internal magnetic field implies the low-spin state of Fe. A structural transition from tetragonal to orthorhombic symmetry appear at at low temperatures (70K-90K) in FeSe.

The spin structure of FeTe is different from that of the FeAs-based parent compounds. The physical properties of FeTe depend on the content of excess Fe at the interlayer site. Furthermore, superconductivity tends to be suppressed with content of excess Fe higher than \( \approx 1.15 \). The samples are almost single phase, however, the superconducting transitions are broad for the primitive polycrystalline samples, implying the existence of the local phase separation. In fact there is a miscible region (A+B), at which phase separations occur, around \( x = 0.7-0.95 \). Using single-phase samples with
x = 0-0.57 it is possible to study crystal structure at low temperatures. With increasing Te concentration, the tetragonal–orthorhombic structural transition observed in FeSe is suppressed. For $FeTe_{0.43}Se_{0.57}$, the structural transition temperature ($T_s$) was determined to be 40 K from synchrotron x-ray diffraction. For $FeTe_{0.507}Se_{0.493}$ tetragonal-orthorhombic transition disappeared, and short-range antiferromagnetic fluctuations were observed with further increase of Te content.

Summarizing, the tetragonal-orthorhombic structural transition observed in FeSe is suppressed with increasing Te concentration. The highest $T_c$ appears at the tetragonal phase near $x = 0.5$. With further increase of Te content, the $T_c$ decreases and in the same time antiferromagnetic ordering accompanying the tetragonal-monoclinic distortion.

The recently discovered Potassium Iron-chalcogenides Recently a new family of Fe-chalcogenide superconductors, with the general formula, $A_xFe_ySe_2$, has been discovered. They show to have significantly enhanced superconducting transition temperatures: $T_c$ up to 32 K (refGuo) as compared to FeSe $T_c \approx 10K$. All of these compounds are multilayered heterostructures containing iron in tetrahedral coordination as is shown in Figure 1.4. The superconducting K-Fe-Se phases is characterized by a $ThCr_2Si_2$-type structure and isostructural with $AFe_2As_2$. The structure determination of AFeSe in this layered tetragonal arrangement was with $A = Tl$. It shows lattice parameters of $a = b = 3.890(1)\,\text{Å}$ and $c = 14.00(1)\,\text{Å}$ and was shown to be a p-type Pauli paramagnetic metal. [4,5]

A related composition was shown to be antiferromagnetic at $T_N \approx 450K$ and have ordered Fe vacancies, which is best described as $TlFe_{2-x}Se_2$ with a $\sqrt{5} \times \sqrt{5} \times 1$ supercell. Superconductivity in potassium iron-selenide shows a $T_c$ of 32 K in $K_xFe_2Se_2$ which has K deficiency, but stoichiometric Fe and Se, and lattice parameters of $a = 3.9136(1)\,\text{Å}$ and $c = 14.0367(7)\,\text{Å}$. 1

Similar properties have also been reported in iron deficient ($Tl,K)Fe_2Se_2$, 28 alkali metal deficient $Rb_{0.8}Fe_2Se_2$, $K_xFe_2Se_2$, and $K_{0.8}Fe_{2.3}Se_2$, and alkali metal and Se deficiency $Rb_{0.78}Fe_2Se_{1.78}$, and $Cs_{0.8}(FeSe_{0.98})_2$. 


Figure 1.4: crystallographic structure of $K_{0.8}Fe_{1.6}Se_2$
Chapter 2

Experimental techniques

2.1 X-ray diffraction

Our understanding of the physics of materials is based upon knowledge of the internal arrangement of the atoms or molecules. Atoms are too small to be imaged directly with electromagnetic radiation and thus our knowledge of the internal structure of materials is based upon diffraction and scattering techniques. As atoms are spaced $\sim 2\text{Å}$ apart we employ radiation of a similar wavelength. The most widely used probes are thus x-rays with a wavelength of $0.1 - 2\text{Å}$.

2.1.1 X-rays sources

X-rays were discovered in 1895 by W. Rontgen as emitting from a cathode ray tube. X-rays are photons of electromagnetic radiation in the wavelength range $\lambda \approx 0.01 - 10\text{nm}$, i.e. photon energies $E \approx 120\text{eV} - 120\text{keV}$ using the relationship

$$E = \frac{hc}{\lambda}; E(\text{keV}) = 12.398/\lambda(\text{Å}) \tag{2.1}$$

**Standard sources**  X-rays are produced when a beam of electrons, accelerated by a high voltage, strikes a metal target. The electrons do not lose their energy in a single collision but through multiple events. The result is the production of a continuous
spectrum of x-rays called white radiation or Bremsstrahlung. Figure 2.1a) shows some continuous x-ray spectra as a function of the accelerating voltage. Note that as the voltage increases so does the minimum wavelength and the total intensity. When the energy of the electrons is higher than a certain threshold value, a second type of spectrum, discontinuous and with very sharp lines, appears superimposed on the Bremsstrahlung. This second spectrum is called the characteristic spectrum because its peaks are found at precisely defined wavelengths dependent only upon the target material. Figure 2.1b) displays the characteristic spectrum of a molybdenum target at 35K. Electrons with sufficient energy can ionise the target atoms by ejection of an electron from one of the atomic inner energy levels. Electrons from higher atomic energy levels then fall down emitting photons with energy corresponding to the difference between the two levels involved. The characteristic lines of this type of spectrum are called K, L and M corresponding to transitions from higher energy orbital to the K, L and M orbital (of principal quantum numbers n = 1, 2 and 3). The $K\alpha$- line corresponds to a transition from the n=2 to the n=1 orbital while the $K\beta$- line originates from the n=3 orbital. The frequency $\nu$ of the characteristic line corresponding to a given transition is related to the atomic number Z of the target material by Moseley’s law, $\nu = C(Z - \sigma)^2$, where the constant $C$ depends on the atomic energy levels involved in the transition and the constant $\sigma$ takes into account the interactions with other electrons. The higher is the atomic number the higher is the characteristic frequency. The two most commonly used characteristic lines are Cu $K\alpha$ (Z = 29) $\lambda = 0.15418\,\text{nm}$ and Mo $K\alpha$ (Z = 42) $\lambda = 0.7107\,\text{Å}$. Laboratory x-ray experiments utilise either sealed-tube or rotating-anode generators. A sealed x-ray tube consists of a cathode with a filament that emits electrons which are accelerated by the high voltage applied. The electrons strike the anode composed of the target material (typically either Cu or Mo) and x-rays are emitted through thin Be windows. The tube is under a high vacuum to avoid scattering of the electrons by air molecules. This process is highly inefficient with only $\sim 0.1\%$ of the applied power being transformed into x-rays. The remaining energy is dissipated as heat and in order to avoid the target melting, the anode is cooled by circulating water. In rotating-anode generators, the target area is continuously renewed because the anode is rapidly rotated. Thus higher powers per unit area can be obtained.
Synchrotron sources  The highest intensities of x-rays are produced by synchrotrons. These are very large particle accelerators in which electrons constrained by magnetic fields circle inside a storage ring with energies of a few GeV. At these energies the particles are relativistic with velocities very close to the speed of light and as they are bent by magnetic fields they emit synchrotron radiation tangentially. This synchrotron radiation can be usefully used as a source of electromagnetic radiation extending from the infrared through the visible and ultraviolet to high energy x-rays. As remarked earlier conventional sources produce characteristic lines at discrete wavelengths. Synchrotron radiation covers the complete x-ray region, depending primarily on the electron energy. It is therefore possible to select any particular wavelength. In addition synchrotron radiation is extremely bright resulting from the small cross-section of the electron beam and the high degree of collimation. An other important property of synchrotron radiation is that it is completely linearly polarised in the plane of the orbit, while X-rays generated from conventional sources are totally non-polarised which require intensity corrections in diffraction experiments. Finally, synchrotron radiation is pulsed with a pulse width of typically 180 ps at 500 MHz. This time periodicity originates from the electrons travelling around the storage ring in bunches, the spacing of which is determined by the radio frequency which is used to restore the electrons energy after emission of synchrotron radiation. The continuous spectrum of the radiation is characterized by its critical wavelength, which divides the spectrum into two parts with equal power (half the power radiated above the critical wavelength and half below). The critical wavelength can be found using the equation below

$$\lambda_c = \frac{4\pi}{3} \frac{E_0^3}{cBE^2}$$ (2.2)

So far we have discussed the radiation emitted by the electrons deflected by bending magnets. At second and third generation synchrotrons, special insertion devices called wigglers and undulators can produce radiation of different characteristics. These are series of periodically spaced magnets of alternating polarity which are inserted in a straight region of the ring. The insertion device creates a sinusoidal magnetic field, which forces the charged particles to oscillate around the mean orbit. A scheme of an
insertion device is shown in Figure 2.2.

The device is described by the k parameter

\[ K = \alpha \gamma = eB_0 \lambda_0 / 2\pi n_0 c \]  

where \( \alpha \) is the maximum deflection angle of the particle trajectory, \( B_0 \) is the oscillating magnetic field measured in T, and \( \lambda_0 \) is the period of the magnetic array measured in centimetres. Recalling that \( 1/\gamma \) is the opening angle \( \Delta \Psi \), \( K \) is the ratio between the maximum deflection angle of the electron trajectory and \( \Delta \Psi \). If \( K \gg 1 \) the device is called wiggler. The effect of a wiggler on the emitted spectrum is to shift the critical energy \( E_c \) to higher values and to increase the intensity of the radiation by a factor proportional to the number of period of the magnetic array. No interference effects are observed between photons generated by different magnetic poles. If \( K \leq 1 \) the device is called undulator and interference occurs between radiations emitted by the same electron at different points in its sinusoidal path. As a result, radiation is emitted as a series of relatively sharp interference peaks whose wavelengths are given by the equation

\[ \lambda_i = \frac{\lambda_0}{2 j^2} \left( 1 + \frac{\alpha^2 \gamma^2}{2} + \gamma^2 \theta^2 \right) \]  

where \( \theta \) is the angle at which radiation is emitted and \( j \) is the harmonic number. As it is evident, the wavelength of the peaks can be shifted by changing the parameters \( \theta \) and \( \alpha \) which is related to \( B_0 \). The intensity produced by an undulator with \( N \) poles at \( \theta = 0 \) is amplified by a factor proportional to \( N^2 \). Insertion devices can, therefore, be efficiently used to substantially increase the flux naturally emitted by a synchrotron and to optimize the spectral range in the hard region of the radiation.

### 2.1.2 Methods

X-ray crystallography is a technique in crystallography in which the pattern produced by the diffraction of X-rays through the closely spaced lattice of atoms in a crystal is recorded and then analyzed to reveal the nature of that lattice. This generally leads to...
Chapter 2. Experimental techniques

Figure 2.1: a) continuous x-ray spectra as a function of different accelerating voltages; b) characteristic spectrum from a molybdenum target due to transitions from higher energy orbital to the K and L orbital.

Figure 2.2: Scheme of an undulator device
an understanding of the material and molecular structure of a substance. The spacing between crystallographic planes in the crystal lattice can be determined using Bragg’s law: there is a Bragg reflection for each crystallographic plane. The electrons that surround the atoms, rather than the atomic nuclei themselves, are the entities which physically interact with the incoming X-ray photons via the Thompson scattering. In Figure 2.3 the Bragg’s law is derived.

The electron density is the Fourier transform of the structure factors $F_{hkl}$. The intensities are proportional to the square of the structure factors $I_{hkl} = K |F_{hkl}|^2$, where $K$ includes several terms, like as the Lorentz (taking into account the time needed by the little volume around the reciprocal lattice node to cross the surface of the reflection sphere) and polarization factors, the incident beam intensity $I_0$, $\lambda^3$ and the volume of the sample. For an accurate structural analysis, one must achieve a representation of the electron density, $\rho(r)$, as good as possible by measuring the intensity $I_{hkl}$ of as many reflections as possible. This can be done in three different ways: 1) using a single crystal and a monochromatic radiation with a fixed direction $S_0$, the crystal is moved so that the most accessible reciprocal lattice nodes are brought to satisfy Bragg’s law. 2) Using a single crystal and a polychromatic radiation each reciprocal lattice node will have a chance of being on the surface of one of the infinite reflection spheres (one for each wave length of the polychromatic radiation) available. 3) A monochromatic radiation with a fixed direction $S_0$, hits a large number of randomly oriented crystals. This is the case of the so-call powder diffraction technique, which will be treated in
more details below.

**Powder diffraction** Ideally, every possible crystalline orientation is represented very equally in a powdered sample. The resulting orientational averaging causes the three-dimensional reciprocal space that is studied in single crystal diffraction to be projected onto a single dimension. The three-dimensional space can be described with (reciprocal) axes $x^*$, $y^*$ and $z^*$ or alternatively in spherical coordinates $q$, $\phi^*$, and $X^*$. In powder diffraction, intensity is homogeneous over $\phi^*$ and $X^*$, and only $q$ remains as an important measurable quantity. In practice, it is sometimes necessary to rotate the sample orientation to eliminate the effects of texturing and achieve true randomness. When the scattered radiation is collected on a flat plate detector, the rotational averaging leads to smooth diffraction rings around the beam axis (Figure 2.4), rather than the discrete Laue spots observed in single crystal diffraction. The angle between the beam axis and the ring is called the scattering angle and in X-ray crystallography always denoted as $2\theta$. (In scattering of visible light the convention is usually to call it $\theta$). In accordance with Bragg’s law, each ring corresponds to a particular reciprocal lattice vector $G$ in the sample crystal. This leads to the definition of the scattering vector as: $q = 2k\sin(\theta) = \frac{4\pi\sin(\theta)}{\lambda}$. Powder diffraction data are usually presented as a diffractogram in which the diffracted intensity $I$ is shown as function either of the scattering angle $2\theta$ or as a function of the scattering vector $q$. The latter variable has the advantage that the diffractogram no longer depends on the value of the wavelength $\lambda$.

**Single Crystal Diffraction** When a crystal is mounted and exposed to an intense beam of X-rays, it scatters the X-rays into a pattern of spots or reflections that can be observed on a detector behind the crystal. The relative intensities of these spots provide the information to determine the arrangement of molecules within the crystal in atomic detail. The intensities of these reflections may be recorded with an area detector or with a charge-coupled device (CCD) image sensor (Figure 2.5). Some measures of diffraction quality can be determined at this point, such as the mosaicity of the crystal and its overall disorder, as observed in the peak widths. Some pathologies of the crystal
that would render it unfit for solving the structure can also be diagnosed quickly at this point. One image of spots is insufficient to reconstruct the whole crystal; it represents only a small slice of the full Fourier transform. To collect all the necessary information, the crystal must be rotated step-by-step through 180°, with an image recorded at every step; actually, slightly more than 180° is required to cover reciprocal space, due to the curvature of the Ewald sphere. However, if the crystal has a higher symmetry, a smaller angular range such as 90° or 45° may be recorded. Each X-ray diffraction image represents only a slice, a spherical slice of reciprocal space, as may be seen by the Ewald sphere construction. Both kout and kin have the same length, due to the elastic scattering, since the wavelength has not changed. Therefore, they may be represented as two radial vectors in a sphere in reciprocal space, which shows the values of q that are sampled in a given diffraction image. Since there is a slight spread in the incoming wavelengths of the incoming X-ray beam, the values of—F(q)—can be measured only for q vectors located between the two spheres corresponding to those radii. Therefore, to obtain a full set of Fourier transform data, it is necessary to rotate the crystal through slightly more than 180°, or sometimes less if sufficient symmetry is present. The recorded series of two-dimensional diffraction patterns, each corresponding to a different crystal orientation, is converted into a three-dimensional model of the electron density; the conversion uses the mathematical technique of Fourier transforms. Each spot corresponds to a different type of variation in the electron density; the crystallographer must determine which variation corresponds to which spot (indexing), the
Figure 2.5: An X-ray diffraction pattern of $K_{0.8}Fe_{1.6}Se_2$ single crystal at 300 K. The pattern of spots (reflections) and the relative strength of each spot (intensities) can be used to determine the structural properties of the system.

relative strengths of the spots in different images (merging and scaling) and how the variations should be combined to yield the total electron density (phasing). Data processing begins with indexing the reflections. This means identifying the dimensions of the unit cell and which image peak corresponds to which position in reciprocal space. A byproduct of indexing is to determine the symmetry of the crystal, i.e., its space group. Having assigned symmetry, the data is then integrated. This converts the hundreds of images containing the thousands of reflections into a single file, consisting of (at the very least) records of the Miller index of each reflection, and an intensity for each reflection.
2.1.3 Uses

Relative to other methods of analysis, powder diffraction allows for rapid, non-destructive analysis of multi-component mixtures without the need for extensive sample preparation. This gives laboratories around the world the ability to quickly analyse unknown materials and perform materials characterization in such fields as metallurgy, mineralogy, forensic science, archeology, condensed matter physics, and the biological and pharmaceutical sciences. Identification is performed by comparison of the diffraction pattern to a known standard or to a database such as the International Centre for Diffraction Data’s Powder Diffraction File (PDF) or the Cambridge Structural Database (CSD). Advances in hardware and software, particularly improved optics and fast detectors, have dramatically improved the analytical capability of the technique, especially relative to the speed of the analysis. The fundamental physics upon which the technique is based provides high precision and accuracy in the measurement of interplanar spacings, sometimes to fractions of an Angstrom, resulting in authoritative identification frequently used in patents, criminal cases and other areas of law enforcement. The ability to analyze multiphase materials also allows analysis of how materials interact in a particular matrix such as a pharmaceutical tablet, a circuit board, a mechanical weld, a geologic core sampling, cement and concrete, or a pigment found in an historic painting. The method has been historically used for the identification and classification of minerals, but it can be used for any materials, even amorphous ones, so long as a suitable reference pattern is known or can be constructed.

Lattice parameters  The position of a diffraction peak is independent of the atomic positions within the cell and entirely determined by the size and shape of the unit cell of the crystalline phase. Each peak represents a certain lattice plane and can therefore be characterized by a Miller index. If the symmetry is high, e.g. cubic or hexagonal it is usually not too hard to identify the index of each peak, even for an unknown phase. This is particularly important in solid-state chemistry, where one is interested in finding and identifying new materials. Once a pattern has been indexed, this characterizes the reaction product and identifies it as a new solid phase. Indexing programs exist to deal with the harder cases, but if the unit cell is very large and the symmetry low (triclinic)
success is not always guaranteed.

**Size and strain broadening** There are many factors that determine the width $B$ of a diffraction peak. These include: 1. instrumental factors 2. the presence of defects to the perfect lattice 3. differences in strain in different grains 4. the size of the crystallites. It is often possible to separate the effects of size and strain. Where size broadening is independent of $q$ ($K=1/d$), strain broadening increases with increasing $q$-values. In most cases there will be both size and strain broadening. It is possible to separate these by combining the two equations in what is known as the Hall-Williamson method:

$$B \times \cos(\theta) = \frac{k\lambda}{D} + \eta \times \sin(\theta),$$

Thus, when we plot $B \times \cos(\theta)$ vs. $\sin(\theta)$ we get a straight line with slope and intercept. The expression is a combination of the Scherrer Equation for size broadening and the Stokes and Wilson expression for strain broadening. The value of $\eta$ is the strain in the crystallites, the value of $D$ represents the size of the crystallites. The constant $k$ is typically close to unity and ranges from 0.8-1.39.

**Phase transitions** At some critical set of conditions, a new arrangement of atoms or molecules may become stable, leading to a phase transition. At this point new diffraction peaks will appear or old ones disappear according to the symmetry of the new phase. If the material melts to an isotropic liquid, all sharp lines will disappear and be replaced by a broad amorphous pattern. If the transition produces another crystalline phase, one set of lines will suddenly be replaced by another set. In some cases however lines will split or coalesce, e.g. if the material undergoes a continuous, second order phase transition. In such cases the symmetry may change because the existing structure is distorted rather than replaced by a completely different one. E.g. the diffraction peaks for the lattice planes (100) and (001) can be found at two different values of $q$ for a tetragonal phase, but if the symmetry becomes cubic the two peaks will come to coincide.
2.2 Scanning nano X-ray diffraction by synchrotron radiation

In the scanning diffractometry setup the entire sample environment is mounted on a hexapod (together with short focal-length optics, when employed). For scanning experiments, a range of different translation and rotation/tilt options are available. A beam monitor installed upstream of the sample (and incorporating an aperture) provides dose-monitoring capabilities and allows on-line exposure normalisation. An on-axis microscope (facing upstream) can be used to visualise the sample in situ at high magnification and design scan regions of interest. Downstream, a selection of detectors are installed on a linear translation stage. The images in Figure 2.6 show the ID13 beamline (at ESRF) scanning setup in detail, configured in this case with short focal-length crossed-mirror optics. However, the whole set-up is highly modular and can be adapted to specific experimental requirements as required. Many of the elements discussed above are annotated on the photographs. That kind of experimental setup allow us to obtain a mixed real- and reciprocal-space images of structural phases ordering. (Figure 2.7 left upper panel) For example the scanning nano X-ray diffraction
Figure 2.7: An example of nanoscale phase separation studied by scanning nano X-ray diffraction at ID13 at European Synchrotron Radiation Facility (ESRF) in Grenoble (Fr)

(nanoXRD) apparatus located at the European Synchrotron Radiation Facility (ESRF) is features an electron undulator providing 12-13-keV X-rays to crystal optics followed by a tapered glass capillary, which produces a 300x300 nm$^2$ beam spot at the sample. A charge-coupled area detector (CCD; right hand side) records the X-rays scattered by the sample. The intensity, I, of structural peaks (or superstructure satellites) due to ordering of lattice phases structure is integrated over square subareas of the images recorded by the CCD detector in reciprocal-lattice units (r.l.u.) and then normalized to the intensity (I0) of the tail of the main crystalline reflections at each point (x, y) of the sample reached by the translator. Lower panel of Figure 2.7 shows an example of phase separation pattern in $K_{0.8}Fe_{1.6}Se_2$ that appears highly inhomogeneous. In this case the intensities of the peaks refferred to the different phases are presented on a linear scale as a colour image. The scale bar corresponds to 600 nm. The intense red–yellow peaks in the two-dimensional colour map represent locations in the sample with prevalence of a phase A, and dark blue indicates spots of prevalence of a phase B. Lower panel of Figure 2.7 is an example of the reconstructed real-space view of the reciprocal-space Intensity distribution of phase A.
Chapter 3

Fe pnictides superconductors

3.1 The effect of internal pressure on the tetragonal to monoclinic structural phase transition in ReOFeAs: the case of NdOFeAs

We report the temperature dependent x-ray powder diffraction of the quaternary compound NdOFeAs (also called NdFeAsO) in the range between 300 and 95 K. We have detected the structural phase transition from the tetragonal phase, with P4/nmm space group, to the orthorhombic or monoclinic phase, with Cmma or P112/n (or P2/c) space group, over a broad temperature range from 150 to 120 K, centered at $T_0 \sim 137$ K. Therefore the temperature of this structural phase transition is strongly reduced, by about $\sim 30$ K, by increasing the internal chemical pressure going from LaOFeAs to NdOFeAs. In contrast, the superconducting critical temperature increases from 27 to 51 K going from LaOFeAs to NdOFeAs doped samples. This result shows that the normal striped orthorhombic Cmma phase competes with the superconducting tetragonal phase. Therefore by controlling the internal chemical pressure in new materials it should be possible to push toward zero the critical temperature $T_0$ of the structural phase transition, giving the striped phase, in order to get superconductors with higher
3.1.1 Introduction

Understanding the quantum mechanism that allows a macroscopic quantum condensate, a superfluid, or a superconductor, to resist the decoherence effects of high temperature is a major topic in condensed matter, quantum computing, and in the search for quantum mechanisms in the living cell. The evidence that in nature it is possible to achieve a quantum condensate of fermions at high temperatures is provided by the so-called high \( T_c \) superconductors. Recent experimental results in this field have added to the known high \( T_c \) superconductors a new class of materials: the layered pnictide-oxide quaternary compounds ReOTmPn (Re = La, Nd, Ce, Sm, . . . ; Tm = Mn, Fe, Co, Ni; Pn = P, As) \[1, 6-15\] where the chemical potential can be driven to a particular point of their electronic phase diagram by controlling the charge density \[1\], the pressure \[9\], the internal chemical pressure \[15\], and the lattice disorder, where a superconducting phase with \( T_c \) as high as 55 K shows up. The electronic and magnetic properties have been investigated \[16-19\] and a particular attention has been addressed to the structural properties of the parent compound LaOFeAs. There have been two experimental reports on the low temperature structure of LaOFeAs \[20, 21\]. Neutron powder diffraction \[20\] and x-ray diffraction \[21\] experiments have demonstrated that LaOFeAs undergoes an abrupt structural distortion below 165 K, changing the symmetry from the tetragonal (space group P4/nmm) to the lower symmetry space group (Cmma or P112/n or P2/c) at low temperature that has been shown to be actually monoclinic. In the neutron study \[20\] it was also reported that the system develops an itinerant antiferromagnetic order with a small magnetic moment (long range spin density wave (SDW)) with a simple stripe-like magnetic structure below the magnetic transition temperature at 130 K. This transition does not show up in superconducting doped samples; therefore it has been suggested that the high \( T_c \) superconducting phase

\[ T_c \]. ¹

occurs in the proximity of a magnetic stripes ordered phase.

3.1.2 Results

These results show that the chemical potential in the stoichiometric parent material is already well tuned to the phase that shows the static magnetic stripes order (like the static stripes phase at 1/8 in Nd doped La2124 samples) and by tuning the chemical potential in the vicinity of this quantum critical point, high $T_c$ superconductivity appears. It is therefore of high interest to investigate the parent stoichiometric compounds of these new high $T_c$ superconductors to study how this stripes phase is dependent on chemical pressure. The recent report on the stoichiometric compound LaFePO has shown that it is not a superconductor, and it does not show the tetragonal to orthorhombic phase transition. In this work we have investigated the stoichiometric system NdOFeAs, in which the FeAs metallic layer suffers a larger compressive microstrain due to the lattice mismatch with the ReO spacer layers in comparison with LaOFeAs sys-
tem. Since the chemical pressure controls the superconducting critical temperature $T_c$ in the doped ReOFeAs systems like in cuprate systems, it is relevant to know the response of the critical temperature of the structural tetragonal to orthorhombic phase transition on the chemical pressure. The NdOFeAs powder samples were synthesized in Beijing, as described elsewhere [11]. The sample consisted of powder of NdOFeAs kept in a 0.5 mm capillary. The temperature of the sample was varied by means of a 700 series Oxford Cryosystems cryocooler with an accuracy of less then 2 K. The x-ray diffraction (XRD) patterns were recorded at the x-ray diffraction beam-line at the Elettra synchrotron radiation facility in Trieste. The x-ray beam emitted by the wiggler source on the Elettra 2 GeV electron storage ring was monochromatized by a Si(111) double crystal monochromator, focused on the sample with a photon energy of 13.760 10 keV (wavelength 0.90105 Å), using a 345 mm ImagePlate based x-ray detector system (Mar345) (Marresearch GmbH, Norderstedt, Germany). As the intensity of the synchrotron radiation beam slowly decreased during the experiment, every diffraction pattern was collected under the condition that the dose of photons scattered by the sample was constant. The two-dimensional patterns collected with the Mar345 were calibrated with silicon crystalline powder and integrated using the software FIT2D. The Rietveld analysis of the XRD powder diffraction patterns was carried out by using the GSAS program. In the range between 300 and 200 K the XRD diffraction pattern of the NdOFeAs shows the typical tetragonal structure with P4/nmm space group. The profile of the 220 line is shown in Figure 3.1. By decreasing the temperature below 200-150 K the line shows an increasing broadening that increases rapidly in the range between 150 and 137 K. The data are fitted with the Cmema space group below 137 K, where we can clearly see the splitting of this line into the two lines of the Cmema space group that are indexed as 040 and 400. The phase transition from tetragonal to orthorhombic phase can be followed by plotting the ratio between the intensity of the XRD diffraction signal at $2\theta_1 = 37.51$ (the center of the 400 line of the Cmema space group) and the intensity at $2\theta_2 = 37.43$ (the center of the 220 line of the P4/nmm space group). The results plotted in Figure 3.2 show that the tetragonal to orthorhombic phase transition, centered at 137 K, is a 30 K wide transition extending from 150 to 120 K, and the 040 and 400 lines are well resolved with our experimental
Figure 3.2: The ratio of the intensity of the XRD diffraction signal at $2\theta_1 = 37.51$ (the center of the 400 line of the Cmma space group) to that at $2\theta_2 = 37.43$ (the center of the 220 line of the P4/nmm space group), probing the broad tetragonal to orthorhombic transition extending from 150 to 120 K; the 040 and the 400 lines are well resolved with our experimental resolution below the critical temperature that is close to 137 K.

resolution only below 137 K. In Figure 3.3 we report the a and b lattice parameters of NdOFeAs as a function of temperature obtained by GSAS fitting. The present results are compared with the data for LaOFeAs reported by Nomura et al [21]. Clearly the chemical compressive internal pressure due to lattice mismatch between the FeAs and ReO layers in NdOFeAs is larger than in LaOFeAs, as is indicated by the shorter Fe-Fe distance. Both systems show a similar tetragonal to orthorhombic phase transition at low temperature. The amplitude of the orthorhombic distortion probed by the difference between the a and b axes in the Cmma phase is similar in the two samples. The main effect of the larger chemical pressure appears to be the decrease of the critical temperature of the structural phase transition.
Figure 3.3: The lattice parameters a and b of NdOFeAs as a function of temperature extracted by GSAS are compared with the lattice parameters of LaOFeAs reported in [21].

3.1.3 Conclusions

In conclusion, we have observed a structural phase transition centered at 137 K in NdOFeAs that is very similar to the phase transition at 165 K in LaOFeAs [21]. Therefore there is a clear evidence that the critical temperature for the structural phase transition associated with the onset of a stripes phase is about 30 K lower than in LaOFeAs. This structural phase transition is similar to the LTO to LTT phase transition in the case of doped cuprates with doping 1/8 and chemical pressure larger than a critical value, that has been identified as the value where two times the $\text{CuO}_2$ microstrain exceeds 8%, associated with the onset of the magnetic stripes order that competes with superconductivity. Therefore we propose that the superconducting doped layered pnictide-oxide quaternary compounds are similar to cuprates in the overdoped phase and the parent undoped systems are similar to the cuprates at doping 1/8 and large microstrain that show the stripes phase. The physical details of this phase transition and the possible phase separation, with the role of the disorder, will deserve further experimental work. This result suggests that the high $T_c$ superconducting phase appears near a
quantum critical point where the striped orthorhombic Cmma phase competes with the superconductive tetragonal phase. Therefore by changing the internal chemical pressure it should be possible to push toward zero the critical temperature of the stripes phase in order to get a superconductor with higher $T_c$.

### 3.2 Structural phase transition and superlattice misfit strain of RFeAsO ($R=\text{La, Pr, Nd, Sm}$)

The tetragonal-to-orthorhombic structural phase transition (SPT) in LaFeAsO (La-1111) and SmFeAsO (Sm-1111) single crystals measured by high-resolution x-ray diffraction is found to be sharp while the RFeAsO ($R=\text{La, Nd, Pr, Sm}$) polycrystalline samples show a broad continuous SPT. Comparing the polycrystalline and the single-crystal 1111 samples, the critical exponents of the SPT are found to be the same while the correlation length critical exponents are found to be very different. These results imply that the lattice fluctuations in 1111 systems change in samples with different surface to volume ratio that is assigned to the relieve of the temperature-dependent superlattice misfit strain between active iron layers and the spacer layers in 1111 systems. This phenomenon that is missing in the $AFe_2As_2$ ($A=$Ca, Sr, Ba) “122” systems, with the same electronic structure but different for the thickness and the elastic constant of the spacer layers, is related with the different maximum superconducting transition temperature in the 1111 (55 K) versus 122 (35 K) systems and implies the surface reconstruction in 1111 single crystals.\(^2\)

#### 3.2.1 Introduction

The natural lattice misfit between first two-dimensional (2D) atomic monolayers and second intercalated spacer layers forming a three-dimensional (3D) superlattice, such as in intercalated graphite, called the superlattice misfit strain (SMS) is known to be a

\(^2\) A. Ricci, N. Poccia, B. Joseph, L. Barba, G. Arrighetti, G. Biasca, J. Q. Yan, R. W. McCallum, T. A. Lograsso, N. D. Zhigadlo, et al. 'Structural phase transition and superlattice misfit strain of RFeAsO ($R=\text{Sm, Nd, Pr, La}$)' Physical Review B 82, 144507+ (2010), URL: http://dx.doi.org/10.1103/PhysRevB.82.144507
key physical variable to describe the physics of these heterostructures at atomic limit. The SMS is of wide use in the study of multilayer semiconductor heterostructures and of a variety of 3D (2D) bulk systems containing 2D (one-dimensional) interfaces. For a given SMS the response of the system depends on the difference between the elastic constant of the first and the second layers, their respective temperature dependence, and the thickness of spacer layers. All-known high-temperature superconductors (HTS), cuprates, diborides, and pnictides, are heterostructures at atomic limit made of first atomic superconducting monolayers intercalated by second layers with variable thickness playing the role of spacers. The SMS is a key physical variable controlling the superconducting critical temperature, \( T_c \), at constant doping in cuprates, diborides, and pnictides. Recently the complex heterogeneity in high \( T_c \) superconducting cuprates, has been related to the SMS that plays a key role in these functional complex systems. In pnictides the \( T_c \) at constant doping shows very large variation as a function of the SMS that induces the deformation of the FeAs lattice, usually measured by the variation of the distance of As ion from the Fe plane. This deformation is due to the variable SMS induced by the variable spacer material since the FeAs layer remains unchanged. The proximity to structural tetragonal-orthorhombic phase transition (SPT) in the undoped pnictides has been identified as a key feature for HTS. The SPT precedes magnetic ordering in the parent RFeAsO (1111) compounds whereas both transitions occur simultaneously in the \( AFe_2As_2 \) (122) compounds [22-24] For the investigation of lattice effects in HTS, it is of high interest to understand the variation in the lattice response as function of the elastic constant and thickness of the spacer layers in the proximity of the SPT [25]. The SMS is expected to induce a microstrain in the active layers that develops a complex lattice structure. The initial studies on the 122 systems indicated the dynamic crystal symmetry breaking to be a second-order phenomena, however, later studies tend to support a picture of a weakly first-order transition and this topic is an object of active investigation. Here, using high-quality single crystals together with corresponding polycrystalline powder samples, we have measured the SPT in the 1111 systems using high-resolution synchrotron x-ray diffraction study of the diffraction intensities and the line-shape broadening.
3.2.2 Experimental details

The single crystals of the 1111 systems are more unstable and difficult to synthesize compared to the 122 compounds. A general method adopted for the synthesis of the 1111 single crystals is using the cubic anvil high-pressure technique. Single crystals of SmFeAsO used in this study were grown under high pressure in NaCl flux while LaFeAsO single crystals were grown under ambient pressure in NaAs flux. We have used one of the best available Sm-1111 single crystals which have around $60 \mu m \times 60 \mu m$ surface area with $10 \mu m$ thickness. Compared to this the La-1111 single crystal was larger with around $2 mm \times 2 mm$ surface area and $10 \mu m$ thickness. The RFeAsO (R=La, Nd, Pr, Sm) polycrystalline samples were prepared by high-pressure synthesis method. The x-ray diffraction (XRD) data on the single crystal samples were obtained at ELETTRA synchrotron radiation facility, Trieste. The data were collected in the K geometry with a photon energy of 12.4 keV using a 2D charged couple device x-ray detector. The sample temperature was varied between 4 and 300 K, and stabilized at the set point waiting for a temperature gradient in the sample to be less than 0.1 K. All the images measured by single-crystal diffraction were properly processed using FIT2D program. The XRD measurements on the polycrystalline powder samples were performed at the Swiss light source facility at PSI, Zurich. The energy resolution was 0.014% with photon wavelength $\lambda = 0.495926 \AA$. Data analysis were performed with the GSAS suite of Rietveld analysis programs.

3.2.3 Results

Figure 3.4 shows the temperature-dependent variation in the unit-cell constants, $a$ and $b$, during the cooling and warming cycles for the La-1111 and Sm-1111 single-crystals and polycrystalline powders, respectively. The high-resolution x-ray diffraction profile of the 220 reflection of the high-temperature tetragonal structure ($P4/nmm$ space group) and the 040 and 400 lines of the low-temperature orthorhombic phase ($Cmma$ space group) of the investigated pnictides are shown in Figure 3.4. To make quantitative analysis, involving the relative intensities and full width at half maximum (FWHM), the peaks were deconvoluted with Gaussian functions. As one lower the temperature, the
Figure 3.4: Upper panels show a (b) lattice constant of the LaFeAsO (left) and SmFeAsO (right) single-crystal samples as a function of temperature during cooling (empty blue circles) and warming (filled red circles) cycle. Middle panels show the same for the corresponding polycrystalline powder samples. Upper insets in these panels show the zoomed region over the SPT indicating the presence of a hysteresis whereas the lower insets in these panels show the evolution of the 220 spot/peak during cooling. Lower panel presents the order parameters for the single crystals and polycrystalline powders during cooling. The order parameter of the $BaFe_2As_2$ system taken from Ref. 22 is shown in the inset for comparison.
diffraction profiles get broader and finally split into two distinct peaks clearly indicating the SPT (Figure 3.4). The nature of the SPT in the single crystals and corresponding polycrystalline powders is described by the order parameter \( OP = \left[ \frac{(a-b)}{(a+b)} \right] \times 10^3 \), where \( a \) and \( b \) are the lattice constants. In Figure 3.4 lower panel, we compare the order parameter (OP) of the single-crystal samples with the polycrystalline powders. Furthermore, the upper insets in all the upper and middle panels of Figure 3.4, clearly indicate the presence of a hysteresis of the structural phase transition in the 1111 systems. The order parameter of the single crystals are sharper than the corresponding polycrystalline powders in its approach toward the SPT critical temperature, \( T_s \). The data corresponding to both single crystal and polycrystalline powder are found to follow a power law with the same critical exponent, \( \beta \) and values 0.25±0.02 for La-1111 and 0.19±0.02 for Sm-1111, respectively. In comparison, the onset of the orthorhombic order is reported to have the \( \beta \) values 0.103±0.018 and 0.112±0.01 in BaFe_2As_2 and EuFe_2As_2, respectively. In fact the same analysis, taking the data from the literature, for the BaFe_2As_2 yields a value 0.136±0.02 (Figure 3.4, inset in the lower panel). The difference between the critical exponents of La-1111 and Sm-1111 from the \((Ba, Eu)Fe_2As_2\) is an index of a different structural coupling of the electronic and lattice strain degrees of freedom in the 1111 and 122 families. The critical exponent of the La-1111 system is \( \beta = 0.25 \), which is quite different from the mean field calculation of the critical exponent \( \beta = 0.5 \). The \( \beta = 0.194 \) found in Sm-1111 is still lower than 0.25 found in La-1111.

A comparison of the variation in the intensity of the 220 peak before and after the SPT, for the single-crystals and polycrystalline powders show remarkable differences, shown in the upper panel of Figure 3.5. As evident from the intensity variation, the SPT occurs over an extended temperature range of about 90 K for the polycrystalline powders, whereas the SPT process is confined within a window of around 20 K in single crystals. Upon cooling-warming cycles, a similar temperature hysteresis, as seen in the lattice constant, is also seen in the intensity plots (not shown). From Figure 3.5, it is clear that the SPT behavior in 1111 single crystals and 122 systems are quite similar. As one approaches the structural transition temperature, the polycrystalline sample due to its finite size increasingly becomes vulnerable to the lattice fluctuations lead-
Figure 3.5: Upper panel: intensity variation of the 220 peak as a function of temperature for the single crystal and polycrystalline powder samples of LaFeAsO (marked as La 1111) and SmFeAsO (marked as Sm 1111) systems together with the intensity variation in a similar peak observed in the BaFe$_2$As$_2$ system (marked as Ba 122 polycrystalline powder). Lower panel: $\Delta\theta/\theta$ of the 220 peak in the tetragonal phase and 400 peak in the orthorhombic phase as a function of $T/T_s$ for the Sm-1111 and La-1111 single crystals (left panel) and polycrystalline powders (right panel). Size of dots shows the dimension of error bar.
ing to an overall broadening of the transition region, resulting in an effective increase in the $T_s$ values of the polycrystalline powders compared to single crystals (see Figure 3.5). The fact that this effect is seen only in the 1111 systems, and not in the 122, implies that the origin of this effect is due to the presence of the spacer layer in the former. The large difference of the lattice fluctuations near a structural phase transition of 1111 samples with different surface to volume ratio show a lattice instability much bigger compared to the 122 systems. It is instructive to compare the evolution of the FWHM of the tetragonal 200 peak and the corresponding orthorhombic peaks (400 or 040), which is shown in Figure 3.5 lower panel. Approaching the $T_s$, the FWHM has longer tail for polycrystalline powder than in singlecrystal samples. It is in fact well known that the widths of diffraction lines are inverse to the sizes of crystallites formed during the material synthesis and that these lines are broadened by microstrain. The difference in the SPT behavior in the single crystal and polycrystalline powder can be understood invoking the idea of larger crumbling of the microcrystallites of the polycrystalline 1111 samples in comparison to the single crystals as one approaches the SPT temperature. In Figure 3.6, we plot the normalized FWHM with the normalized temperature for the polycrystalline powders and single crystals. The results for the PrFeAsO and NdFeAsO polycrystalline powder samples are also shown. For temperature below $T_s$, the normalization is done by taking the value of the FWHM at $0.3 \times T_s$ to unity (Figure 3.6 lower panel), while for temperatures above $T_s$, the normalization is done by taking the FWHM values at $1.7 \times T_s$ to unity. The correlation length $\xi$ (has an inverse relation with FWHM) of the line-shape approaching $T_s$ is well described by a power law $\xi^{-1} = t^\nu$, where $t$ is the reduced temperature (defined in Figure 3.6). Although both single crystals and polycrystalline powders are found to follow the $\xi^{-1} = t^\nu$ power law, the corresponding exponent, $\nu$, for the polycrystalline powder and the single crystal are found to be very different for the identical system, the later being four times higher. Such powder-law fits for the polycrystalline powders of La-1111, Pr-1111, Sm-1111, and Nd-1111 are shown in the upper panels of Figure 3.6. In the case of the polycrystalline powder samples, the exponent increases almost linearly with increasing rare-earth ionic size (see Figure 3.6 lower panels). Marked difference in the correlation length exponents observed in the case of the polycrystalline powder
and the corresponding single crystals is an evidence of the crystallite size-dependent SMS effects in the 1111 system. However both 1111 materials (grown with two different procedures) show different lattice fluctuations going from microcrystallines of powders (diameter less than $1\mu m$) to larger single crystals.

### 3.2.4 Discussion and Conclusions

The difference between the small grains and large single crystals is attributed to the difference between the elastic constant of active FeAs and rare-earth oxide spacer layers. In 1111 polycrystalline systems the surface of grains is expected to be different since the surface layer has a different elastic strain compared to the layers in the bulk. On the contrary, the 122 systems show similar lattice response for the small (polycrystalline powder) and for large crystals indicating that the surface to volume ratio does not play a significant role in 122 systems and the elastic stress due to the natural interlayer misfit is different. This difference in the lattice response could be related to the unexplained difference of the superconducting critical temperature between 1111 and 122 samples having similar electronic structure.

In conclusion, the structural phase transition in the La-1111 and Sm-1111 appears to be a case of intermixing of first- and second-order transitions that in correlated materials is not rare. The comparison between the x-ray diffraction data for the polycrystalline 1111 samples and the single crystals shows a relevant differences as one approach the SPT temperature. This is assigned to an elastic response dependence of the surface to volume ratio of the sample. Difference in the $\beta$ exponent and the temperature dependence of the single crystal and polycrystalline powder data underline the importance of the superlattice misfit strain in the phase diagram and for the functional properties of these heterostructures at atomic limit. The 122 systems on the contrary show the same lattice fluctuations in microcrystals and large crystals. This difference (between the 1111 and 122) is assigned to the difference between the elastic constant of the spacer layers in the two systems. The electronic structure of 1111 and 122 systems is very similar so this difference in the dynamical response between the 1111 and 122 systems may explain the increase in the $T_c$, from 35 K in 122 to 55 K in 1111.
Figure 3.6: Normalized FWHM of the tetragonal 220 peak and corresponding orthorhombic 400 (or 040) peak as a function of temperature for the RFeAsO (R=La, Pr, Sm, Nd) systems. $T < T_s$ and $T > T_s$ are shown in the left and right panels, respectively. Upper panel compares the behavior of the polycrystalline powder samples. Middle panels compare the normalized FWHM of the single-crystal and polycrystalline powder systems. Fit to the data are included as lines. The exponents obtained from the fits are compared in the lower panels as a function of the rare-earth ionic size. Size of dots shows the dimension of error bar.
systems in fact the misfit strain has been proposed to be the key term determining the critical multiscale phase separation in doped high-temperature superconductors giving the so-called superstripes scenario.
Chapter 4

Fe chalcogenide superconductors

4.1 Intrinsic phase separation in superconducting $K_{0.8}Fe_{1.6}Se_2$ ($T_c = 31.8$ K) single crystals

Temperature dependent single-crystal x-ray diffraction (XRD) in transmission mode probing the bulk of the newly discovered $K_{0.8}Fe_{1.6}Se_2$ superconductor ($T_c = 31.8K$) using synchrotron radiation is reported. A clear evidence of intrinsic phase separation at 520 K between two competing phases, (i) a first majority magnetic phase with a $ThCr_2Si_2$-type tetragonal lattice modulated by the iron $\sqrt{5} \times \sqrt{5}$ vacancy ordering and (ii) a minority non-magnetic phase having an in-plane compressed lattice volume and a $\sqrt{2} \times \sqrt{2}$ weak superstructure, is reported. The XRD peaks due to the Fe vacancy $\sqrt{5} \times \sqrt{5}$ ordering in the majority phase disappear on increasing the temperature to 580 K, well above phase separation temperature, confirming the order-disorder phase transition. The intrinsic phase separation at 520 K between a competing first magnetic phase and a second non-magnetic phase in the normal phase both having lattice superstructures (that imply different Fermi surface topology reconstructions and charge densities) is assigned to a lattice-electronic instability of the $K_{0.8}Fe_{1.6}Se_2$ system typical of a system tuned at a Lifshitz critical point of an electronic topological transition that gives a multigap superconductor tuned to a shape resonance.  

1 A. Ricci, N. Poccia, B. Joseph, G. Arrighetti, L. Barba, J. Plaisier, G. Campi, Y. Mizuguchi, H. Takeya, Y. Takano, et al., 'Intrinsic phase separation in superconducting $K_{0.8}Fe_{1.6}Se_2$'
4.1.1 Introduction

The discovery of iron-based superconductors (FeSC) made of FeAs superconducting layers intercalated by different spacer layers [26, 27] has provided a new class of heterostructures at the atomic limit where the lattice structure and its instability are key parameters controlling the complex Fermi surface topology giving multigap superconductivity stable at high temperature. Recently a new system $A_xFe_{2-y}Se_2$, made of FeSe superconducting layers intercalated by spacer layers $A = K$ [4, 28], Cs [29, 30], Rb [31], (Tl, Rb) [32], (Tl, K) [33], etc, has provided an additional system with a different Fermi surface topology. The most striking common feature of the FeSC is the presence of an active layer of FePn or FeCh (Pn: pnictogen and Ch: chalcogen) edge sharing tetrahedrons. The $A_xFe_{2-y}Se_2$ show multigap superconductivity with concentric multiple Fermi surfaces as has been proposed in the shape resonance scenario for multigap superconductors made of heterostructures at the atomic limit [34]. Heterostructures of metallic layers at the atomic limit provide metals with mini bands where high $T_c$ is controlled by the fine tuning of the chemical potential in the range of tens to hundreds of meV around Lifshitz electronic topological transitions [34]. At such a low energy scale the fine tuning of the lattice structure of the superconducting active layers in these heterostructures at the atomic limit is of high importance. The structure of the active superconducting layers is controlled by changing the spacer layers via the misfit strain between the active layers and the spacer layers as in cuprates [35]. The average crystal structure of $A_xFe_{2-y}Se_2$ at room temperature has already been established by different structural studies [12–19]. These studies revealed the structure of $A_xFe_{2-y}Se_2$ to be of ‘122’ type, with the presence of a Fe-square lattice decorated by a regular array of vacancies [5, 36–42] and hence a unit-cell structure five times larger than the basic $ThCr_2Si_2$ - type tetragonal unit-cell. Figure 4.1(B) shows a schematic view of the basic ‘122’ type unit-cell and an expanded cell which can accommodate ordered vacancies at one of the Fe- sites. Temperature dependent neutron diffraction studies have revealed that the structural and magnetic phase transitions are related with the vacancy ordering in this system [37, 38, 41]. Here we present a tem-

temperature dependent single-crystal x-ray diffraction study of the $K_{0.8}Fe_{1.6}Se_2$ superconductor ($T_c = 31.8K$) to understand the structural dynamics of the system. We use high energy x-ray synchrotron radiation diffraction in transmission mode which allows us to probe the intrinsic bulk structure. We confirm previous works showing that the system undergoes an order–disorder transition at 580 K, as evidenced by the disappearance of the superstructure peaks due to the vacancy ordering. The superstructure peak intensities follow the same behavior upon heating and cooling with no detectable temperature hysteresis. The main discovery of this work is that, unlike the earlier diffraction studies using powder samples [13, 14], our high-resolution single-crystal x-ray diffraction data show the occurrence of a phase separation in $K_{0.8}Fe_{1.6}Se_2$ below 520 K (about 60 K lower than the vacancy ordering temperature) between a first in-plane expanded majority phase and a second in-plane compressed minority phase. Moreover, on decreasing the temperature below 520 K a new set of superstructure diffraction peaks associated with the appearance of the minority phase is observed. These results constitute clear evidence of an intrinsic phase separation in the 122 chalcogenides $K_{0.8}Fe_{1.6}Se_2$, which is assigned to the lattice instability of an electronic system near a Lifshitz critical point where a majority magnetic phase competes with the superconducting multigap phase where $T_c$ is amplified by a shape resonance [34]. The competition between the two phases provides a complex phase separation where the two lattice structures show different lattice reconstructions.

4.1.2 Experimental details

Single crystals of nominal composition $K_{0.8}Fe_{1.6}Se_2$ were prepared following the method described in [28]. The actual composition of the crystal was estimated to be K : Fe : Se = 0.6 : 1.5 : 2 using an average of four points of the EDX measurements. The resistivity and magnetization studies showed the presence of a sharp superconducting transition at about 31.8 K ($T_c$ onset 33 K) [28]. The x-ray diffraction (XRD) data on the single-crystal samples were obtained at the XRD1 beamline of the ELETTRA synchrotron radiation facility in Trieste. The samples were oriented by means of a K diffractometer with a motorized goniometric X-Y stage head and a Mar-Research
Figure 4.1: Single-crystal x-ray diffraction pattern (CCD image) of $K_{0.8}Fe_{1.6}Se_2$. Structural models of the basic (I 4/mmm) and larger (I 4/m) unit-cells of the 122-type tetragonal structure are also shown.

165 mm CCD camera. The data were collected in transmission mode, with a photon energy of 20 keV ($\lambda = 0.61992\,\text{Å}$), selected from the source by a double-crystal Si(111) monochromator. The x-ray diffracted beams were detected by a 2D CCD detector (MAR-Research), kept at a distance of around 70 mm from the sample. Data from a LaB$_6$ standard were also collected for calibration. Measurements were conducted between 80 and 600 K with a temperature step of 3 K for the heating (80-600 K) and 2 K for the cooling (600-80 K) runs. For the measurements in the range of 80-300 K, the sample temperature was varied and controlled by means of a cryocooler (700 series Oxford Cryosystems). For the measurements in the temperature range 300-600 K, a heat blower facility (Oxford Danfysik gas blower, DGB-0002) was used. In both cases, the temperature control was better than $\pm 1\,\text{K}$. The single-crystal x-ray diffraction images measured were properly processed using the FIT2D program. The processed images were analyzed using a MATLAB based software package developed in-house.
Figure 4.2: (Upper panel) temperature evolution of the spots due to superstructures around the beam center at five selected temperatures. The first set of superlattice peaks ($\sqrt{5} \times \sqrt{5}$) are marked with open circles and the second set of weak superstructure peaks ($\sqrt{2} \times \sqrt{2}$) are marked by squares. Starting from high temperature, at 600 K there are no superstructure spots, at 525 K only the first set of superstructure is detected, and in the frames recorded at 510 K and lower temperatures both superstructures are detected. (Lower panel) the intensity of the superstructure peaks (of the first $\sqrt{5} \times \sqrt{5}$ type, marked with circles in the upper panel) during a heating run from 80 to 600 K. The inset shows the superstructure peaks (of the first $\sqrt{5} \times \sqrt{5}$ type, marked with circles in the upper panel) as a group of eight spots around the (100) peak position.
4.1.3 Results

A typical single-crystal XRD as-obtained pattern at 300 K is shown in Figure 4.1. The pattern at room temperature is similar to the one reported in [5] for a similar compound. The crystal displays a tetragonal $ThCr_2Si_2$-type diffraction pattern with overlapping superstructure peaks. Structural models corresponding to the basic and extended unit-cells are also shown in Figure 4.1. The extended unit-cell has two sites for the Fe (4d and 16i), which permits the vacancies to preferentially occupy one of the sites and order. The vacancy ordering observed at room temperature gives rise to the superstructure diffracted spots that can be indexed with a $\sqrt{5} \times \sqrt{5} \times 1$ expanded unit-cell (symmetry $I\ 4/m$) of the basic $ThCr_2Si_2$ structure [37-41]. The a, b lattice parameters corresponding to the basic unit-cell are determined from the pattern shown in Figure 4.1. The obtained value is $a = b \approx 4.01(3)$ Å. A careful observation of the image shown in Figure 4.1 reveals that the principal diffraction spots are surrounded by superstructure peaks forming a group of eight reflections (see inset in Figure 4.2 lower panel) in agreement with the data reported for similar systems at room temperature. Diffraction patterns with superstructure peaks around the beam center, at five selected temperatures, are shown in the upper panel of Figure 4.2. At 600 K, except for the principal diffraction spots, there are no other superstructure features. The data collected at 525 K show a single group of bright spots in Figure 4.1a that can be clearly identified as belonging to the group of eight superstructure reflections around each principal XRD spot (see e.g., the inset in Figure 4.2) identified as the (1/5, 3/5, 0) diffraction spots in the reciprocal space. The occurrence of eight well defined superstructure spots can be understood as the twin structure described in [41]. The peak intensity variation for one of the superstructure peaks of the first type during the heating run from 80 to 600 K is shown in the lower panel of Figure 4.2. On increasing the temperature, the intensity of these superstructures starts to slowly decrease at around 520 K and finally disappears at around 580 K. In addition to the first known set of superstructure peaks, we observe the appearance of a second new set of superstructure peaks below 520 K (see Figure 4.2, upper panel, frame marked as 510 K), assigned to the $\sqrt{2} \times \sqrt{2}$ superstructure. Figure 4.3 shows the temperature evolution of the (220) principal diffraction peaks.
spot. Below 520 K, the peak splits into two components with asymmetric intensities that become more evident in the low temperature range. The complete evolution of the (220) peak between 300 and 600 K during the heating run, reconstructed from the CCD image analysis, is shown in the middle panel as a 3D plot of intensity versus temperature and reciprocal lattice wavevector. A clear peak splitting is evident below 520 K. The relative intensities of the diffraction spots of the two crystal lattices permit us to make a rough estimate of the percentage of the two phases. The bottom panel of Figure 4.3 shows the change in the normalized intensities of the majority in-plane expanded phase and the minority in-plane compressed phase. The majority phase has a weight of about 79% at 350 K which becomes 100% at the same temperature due to the in-plane compressed minority phase. These data show clearly the intrinsic phase separation in the $K_{0.8}Fe_{1.6}Se_2$ superconductor below 520 K. In Figure 4.4, we summarize the results of the present study. During cooling from the disordered single phase at 600 K, the superstructure peaks due to $\sqrt{5} \times \sqrt{5}$ vacancy ordering start to appear at around 580 K, at the same temperature as these peaks disappear in the heating run. In other words, the temperature dependence of the peak intensity variation seems to be identical in the heating and cooling runs. In contrast, the peak intensity of the (220) satellite during the heating and cooling shows a sharp intensity drop at about 520 K, with a temperature hysteresis of about 10 K. This implies that the intrinsic phase separation occurring at this temperature is primarily of first order nature, unlike the continuous second order nature of the superstructure peak transition at 580 K. Importantly, the superstructure peak intensity shows no particular change at the phase separation temperature of 520 K. However, as shown in Figure 4.2, a new set of $\sqrt{2} \times \sqrt{2}$ superstructure peaks starts to appear at 520 K. The temperature dependence of the integrated intensities of these new superstructure peaks in a limited temperature range during a cooling run is shown in the inset of the left panel in Figure 4.4. The principal diffraction spots of the minority in-plane compressed phase and the new set of $\sqrt{2} \times \sqrt{2}$ superstructure peaks appear at the same temperature, indicating an intimate connection between the two. Further work is ongoing to characterize this superstructure and it will be the subject of a longer paper.
Figure 4.3: (Upper panel) temperature evolution of the (220) peaks at five selected temperatures. (Middle panel) a three-dimensional intensity plot of the (220) peak as a function of temperature for the heating run from 300 to 600 K. Below 520 K, the (220) peaks split, indicating the appearance of a second in-plane compressed minority phase. (Lower left panel) the normalized peak intensities of the first main phase and the second minority phase. (Lower right panel) the in-plane lattice parameter variation with temperature showing the phase separation at 520 K.
Figure 4.4: (Left panel) the continuous temperature evolution of the $\sqrt{3} \times \sqrt{3}$ superstructure satellite intensity during the heating (open triangles) and cooling (filled squares) runs. The sharp temperature drop of the minority phase during the heating (open squares) and its appearance on cooling (open circles) runs can be seen. The inset in the left panel shows the temperature dependence of the integrated intensities of the second weak set of $\sqrt{2} \times \sqrt{2}$ superstructure peaks (filled squares) (refer to the spots in the open squares in figure 2). During the cooling run the $\sqrt{2} \times \sqrt{2}$ superstructure peaks show the same temperature onset as the principal XRD diffraction spots of the minority in-plane compressed phase. (Right panel) the variation of the probability of the minority in-plane compressed phase around the phase separation temperature (520 K) (filled dots) and the temperature variation of the ratio (open circles) between the intensity of the $\sqrt{5} \times \sqrt{5}$ iron vacancy superstructure satellites and the principal diffraction spots of the in-plane expanded majority phase.
4.1.4 Discussion and Conclusions

We first discuss the ordering of iron vacancies in the majority in-plane expanded phase. The first thing to notice is that the temperature evolution of the associated $\sqrt{5} \times \sqrt{5}$ superstructure spots is in agreement with previous neutron diffraction studies [37, 38] on similar systems. The Neel temperature estimated from the neutron diffraction studies is around 560 K, below the order–disorder transition observed at 590 K [37, 38], thus presenting a close analogy between the structural and magnetic transitions observed in the ‘1111’ family of FeSCs and the new $A_xFe_{2-y}Se_2$ systems. Interestingly, the magnetic and structural transitions are concurrent in the structurally identical ‘122’ pnictides. As already discussed, the temperature dependence of the appearance and disappearance of the $\sqrt{5} \times \sqrt{5}$ superstructure is continuous, without a significant temperature hysteresis, indicating the transition to be of second order. Let us now discuss the new intrinsic phase separation observed here. Earlier structural studies using powder samples [37, 38] have not revealed such a transition in $A_xFe_{2-y}Se_2$ superconductors. Indeed single-crystal studies provide more insights into the phase separation properties, as revealed in the case of ‘1111’ FeSCs. It is to be stressed that there is the simultaneous sharp appearance of a new set of superstructure peaks together with the minority in-plane compressed phase by decreasing the temperature to below 520 K. A recent 57 Fe Mossbauer study on the $K_xFe_{2-y}Se_2$ system revealed abrupt changes in the magnetic fraction of the sample at about a similar temperature to the phase separation observed here. The temperature evolution of the magnetic fraction observed in the Mossbauer studies of $K_xFe_{2-y}Se_2$ is also of similar nature. These results indicate the existence of two coexisting phases in the low temperature region of $K_xFe_{2-y}Se_2$. Very recent differential scanning calorimetric measurements on superconducting $Cs_xFe_{2-y}Se_2$ show two distinct heat-flow peaks, a larger one at higher temperature and a weaker one at lower temperature [41], further supporting two possible phases in superconducting $K_xFe_{2-y}Se_2$. The present observation of the intrinsic phase separation in $K_xFe_{2-y}Se_2$ indicates the importance of the lattice complexity of the $A_xFe_{2-y}Se_2$ systems. Indeed the phase diagram involving Fe-Se shows the possibility of coexisting phases for different ratios between Fe and Se, consistent with the
extreme sensitivity of the chemical composition to the superconducting properties of FeSe. The coexisting chalcogen heights observed in the doped ternary chalcogenides are found to be more pronounced in the $A_xFe_{2-y}Se_2$ systems [39-41]. The $K_xFe_{2-y}Se_2$ system with its interesting temperature dependent vacancy ordering and competing mesoscopic phases recalls the oxygen ordering effects on the superconductivity of cuprates. This intrinsic phase separation is assigned to a generic feature of multigap high temperature superconductors where the system is on the verge of phase separation like in FeAs superlattices [29] and cuprates [30-37]. The data show a clear case of the competition between two electron fluids producing a mesoscopic frustrated phase separation between a majority magnetic metallic phase with $\sqrt{5} \times \sqrt{5}$ ordered defects and a superconducting phase with a second $\sqrt{2} \times \sqrt{2}$ superstructure order with different charge densities; i.e. two striped metallic systems with two different lattice superstructures that will induce a different Fermi surface reconstruction with mini bands and pseudogaps of a few tens of meV. The present scenario for $A_xFe_{2-y}Se_2$ is similar to the case of overdoped cuprates where two phases compete with different dopings [35-38].

We have reported temperature dependent single-crystal x-ray diffraction studies of the newly discovered $K_xFe_{2-y}Se_2$ superconductor using synchrotron radiation in transmission mode. The basic structure of the sample at room temperature is found to be tetragonal $ThCr_2Si_2$-type, modulated by vacancy ordering induced superstructures together with a coexisting minority phase with associated different superstructures. The phase separation appears at 520 K, above which the minority in-plane compressed phase merges with the majority in-plane expanded phase. There is a temperature hysteresis of about 10 K, indicating the phase separation transition to be first order. The superstructure peaks corresponding to the main Fe vacancy ordering disappear at 580 K, without noticeable temperature hysteresis, confirming the order–disorder second order phase transition at high temperatures above the phase separation temperature. The present scenario shows that a heterostructure at the atomic limit made of a superlattice of metallic layers like iron based superconductors tuned at a Lifshitz critical point [34], is on the verge of a lattice catastrophe for phase separation between the two types of metals. In the phase separation regime a fine tuning of their Fermiology via two lat-
tice superstructures provides a first itinerant magnetic phase with low lattice symmetry and a second high temperature superconductor tuned at a shape resonance [34] in a landscape of complex phase separation that was called the ‘superstripes’ scenario in cuprates.

4.2 Nanoscale phase separation in the iron chalcogenide superconductor $K_xFe_{2-y}Se_2$ as seen via scanning nano-focused x-ray diffraction

The advanced synchrotron radiation focusing down to a size of 300 nm has been used to visualize nanoscale phase separation in the $K_xFe_{2-y}Se_2$ superconducting system using scanning nano-focus single crystal X-ray diffraction. The results show an intrinsic phase separation in $K_xFe_{2-y}Se_2$ single crystals at $T \geq 520$ K, revealing coexistence of; i) a magnetic phase characterized by an expanded lattice with superstructures due to Fe vacancy ordering and; ii) a non-magnetic phase with an in-plane compressed lattice. The spatial distribution of the two phases at 300 K shows a frustrated or arrested nature of the phase separation. The space resolved imaging of the phase separation permitted us to provide a direct evidence of nano phase domains smaller than 300 nm and different micron size regions with percolating magnetic or non-magnetic domains forming a multiscale complex network of the two phases.²

4.2.1 Introduction

Has been shown that $A_xFe_{2-y}Se_2$ chalcogenide superconductors show both high temperature superconductivity and magnetism. In these compounds, one may tune the interplay of superconductivity and magnetism by changing the Fe-vacancy order and the superlattice misfit strain [44]. The open question to be answered is whether there is a coexistence of magnetism and superconductivity in the same spatial region or these

² A. Ricci, et al., 'Nanoscale phase separation in the iron chalcogenide superconductor $K_{0.8}Fe_{1.6}Se_2$ as seen via scanning nanofocused x-ray diffraction' Physical Review B 84, 060511+ (2011), URL http://dx.doi.org/10.1103/PhysRevB.84.060511
phenomena occur in different spatial regions dictated by the phase separation. Opposite conclusions have been drawn by different groups using different experimental methods, some favouring the coexistence, while others the phase separation. The phase separation appears on multiple scales from micron-scale to nano-scale in cuprates [45-47], diborides [48] and pnictides [49]. Several theories [22-30] have described the complex phase separation as an intrinsic feature of all known HTS.

X-ray diffraction (XRD), the most direct probe of phase separation, has revealed phase separation in undoped magnetic phase and non-magnetic phase in an underdoped $La_2CuO_4+y$ system [46]. The phase separation in an overdoped $La_2CuO_4+y$ system has been observed recently by scanning micro x-ray diffraction [47] to simultaneously probe both real and reciprocal spaces. Here we report evidence of frustrated phase separation in $A_xFe_{2−y}Se_2$ with domains of magnetic phase, characterized by expanded lattice with $\sqrt{5} \times \sqrt{5} \times 1$ ordered superstructure of iron vacancies, and domains of in-plane compressed non-magnetic phase. Using conventional high-energy x-ray diffraction and advances in focusing x-ray synchrotron radiation we have been able to probe both the average bulk structure and to map of the phase separation on nanometre scale in the same sample.

4.2.2 Experimental details

The experimental set-up used for the single crystal diffraction studies in the transmission mode (probing the average bulk structure) and the reflection mode (nano-focus beam scanning for mapping the phase separation) is shown in Figure 4.5. The single crystals of $K_xFe_{2−y}Se_2$ were grown by melting a precursor of FeSe and K (in nominal composition of 2:0.8) placed in an alumina crucible that was sealed into an arc-welded stainless-steel tube. The sample went through a heating treatment at 1030°C for 2 h followed by a slow cooling down to 750°C with a rate of 6°C/h. We obtained plate-like and dark-shining single crystals. The details on the crystal growth can be found in ref. [28]. The obtained crystals were characterized for their phase purity using in-house x-ray diffraction measurements. The chemical compositions of these crystals were determined by energy dispersive x-ray analysis (EDX), and found to be nearly
Figure 4.5: (panel A) X-ray diffraction set up in transmission mode at the XRD1 beamline at the ELETTRA synchrotron radiation facility providing the CCD image of the x-rays reflections on the $K_xFe_{2-y}Se_2$ obtained at room temperature. A zoom over the (220) peak is shown in panel B, revealing co-existing phases in $K_xFe_{2-y}Se_2$ evidenced by the splitting of the (220), one with a smaller in-plane lattice parameters (called compressed phase) and one with the longer lattice parameter (called expanded phase). (panel C) Diffraction profile of the (220) reflection is shown. X-ray diffraction image obtained in reflection mode is shown in panel D. A zoom over the (0012) reflections is also shown (panel E). Peak profile of the (0012) reflection in the c-direction is shown, revealing a clear phase separation in the c-axis (panel F).
equal to the nominal with slight variations between different crystals obtained from the same batch. Temperature dependent magnetization and resistivity measurements were performed using a SQUID magnetometer and a four-probe system respectively. The single crystals show sharp superconducting transition temperature around 32 K. For the synchrotron radiation x-ray diffraction measurements, reported in this work, we used a small piece of a large plate-like single crystal with a $T_c = 31.8K$, that was well characterized for its phase purity and composition. The single crystal diffraction profiles were found to be very sharp, ascertaining high quality of the crystal used in the present study. We first present results on the phase separation observed in the temperature dependent (80-600 K) single crystal XRD (in transmission mode), probing a 105 micron depth bulk sample i.e. a volume of $200 \times 200 \times 105 \mu m^3$. Figure 4.6 shows the results of the temperature dependent single-crystal x-ray diffraction measurements, conducted at the XRD1 beamline of the ELETTRA synchrotron radiation facility, Trieste, using photons of energy 20 KeV.

4.2.3 Results

The crystal symmetry at 600 K is found to be of tetragonal (space group I4/mmm, $ThCr_2Si_2$-type tetragonal unit-cell) with lattice parameters $a=b=0.401$ nm and $c=1.384$ nm. Below 580 K, superlattice peaks start to appear indicating the Fe vacancy ordering. This vacancy ordered structure, called A phase, and described by several groups, has been associated with the magnetic order [30, 38]. The system undergoes an intrinsic phase separation below 520 K with the appearance of a new phase with slightly compressed basal lattice parameters ($a, b$). The Figure 4.6 shows the splitting of the (220) reflection at variable temperature. The appearing phase has 2.5% shorter in-plane lattice parameters and about 1% expanded c-axis, called the in-plane compressed phase (B phase). The probability of the phase B turns out to be about 20 – 30% averaged over a volume of $4.2 \times 10^{15} nm^3$. To study the nanoscopic spatial distribution of the intrinsic phase separation, we have obtained sample imaging at room temperature after a slow cooling rate of 0.1K/min from 530K. We have measured the x-ray diffraction in the reflection mode using a $300 \times 300 nm^2$ beam size with a penetration depth of re-
Figure 4.6: (panel A) A 3D color plot of the temperature dependence of the (220) reflection measured on the $K_xFe_{2−y}Se_2$ single crystal. A clear phase separation in a compressed phase (shorter a, b parameters) phase and an expanded (longer a, b lattice parameters) phase appears below 520 K. (panel B) Temperature dependence of in-plane difference of the tetragonal a, b lattice parameters between the compressed and the expanded phase recorded with a cooling rate of 0.1K/min.
reflected x-rays of about 11 micron. Thus the volume of the probed surface for a single
diffraction pattern is about \(9.9 \times 10^8\) nm\(^3\), i.e., about \(2.3 \times 10^7\) times smaller than the
volume probed by the transmission x-ray diffraction.

Figure 4.7 displays the (0016) reflections at three different positions of area \((300 \times
300\) nm\(^2\)) each on the single crystal \(K_xFe_{2-y}Se_2\) surface at 300 K. Within the same
\(9.9 \times 10^8\) nm\(^3\) crystal surface-volume illuminated by the x-ray beam we probe a dif-
f erent phase separation inside the illuminated volume given by the ratio between the
(0016) reflection intensities due to the phase A and the phase B, showing large changes
from site to site. Figure 4.8 shows the spatial mapping of the ratio of the two phases,
revealing changes from spot to spot. There are regions where the B phase is dominant
and other large regions where the A phase is the dominant one.

Figure 4.8 shows two such regions of the \(K_xFe_{2-y}Se_2\) crystal of size \(22 \times 55\) µm\(^2\) mapped using scanning x-ray nano-focus diffraction in reflection mode. The intense
red-yellow peaks in the two dimensional color maps (Figure 4.8) represent locations
with predominance of the B phase. In particular, the two maps show an over all weights
for the B-A phase to be of 50 – 50% and 30 – 70% respectively. This value appears to
be consistent with the values estimated using x-ray diffraction in transmission mode,
probing a much larger bulk volume (with values to be almost 30 – 70%).

4.2.4 Discussion and Conclusions

The present observation of an intrinsic phase separation with the co-existence of an
expanded and a compressed phase suggests the importance of inhomogeneity in the
\(A_xFe_{2-y}Se_2\) systems. To have an estimate of the coherence length associated with
the domains of the two phases, we have used deconvolution of the peak profiles (Figure 4.7 lower panel). The extracted domain size from the peak profile analysis,
measured by the diffraction coherence length, is found to be about 6 nm. This small
size of the homogenous phase points towards a frustrated nanoscale phase separation.
Moving the nano x-ray beam on the sample surface we find that the ratio between the
intensity of the reflections probing the ratio between the compressed B phase and the
A phase changes in a dramatic way. As can be seen in the Figure 4.7, the relative prob-
Figure 4.7: (panel A) The reciprocal 3-dimensional view of the x-ray reflections around (0016) of the $K_xFe_{2-y}Se_2$ measured at the ESRF using a 300 nm focused beam. Reflections from three different regions of the sample are shown, revealing variable strength of the expanded and compressed phases at different spatial locations. (panel B) The corresponding 2D profiles along the $c^*$-direction are shown. The diffraction coherence length estimated from the full width at half maximum (FWHM) of the reflection profiles is found to be $\approx 6 nm$. 


Figure 4.8: Panel A shows the spatial distribution of ratio of the compressed and the expanded phase in regions of size $22 \times 55 \mu m^2$ of the $K_xFe_{2-y}Se_2$ crystal. The crystallographic a-axis and b-axis are along the horizontal and the vertical directions. The intensity of the compressed phase, $I(c)$, and of the expanded phase, $I(e)$ is integrated over square subareas of the image recorded by the CCD detector in reciprocal-lattice (r.l.u) and their ratio $\frac{I(c) - I_0}{I(e) - I_0}$ is plotted at each (x,y) point of the sample surface. The intense yellow peaks in the two-dimensional color map represent locations of the sample with dominant compressed phase, black indicates spots of dominant expand phase.

Panel B shows the frequency (arbitrary units) of the ratio values between the compressed and the expanded phase in different surface regions (relative volume of collapsed phase) is plotted for the first (blue filled circles) and second (red empty square) surface region, representing distribution in different region.
ability of the compressed versus expanded phase is about 30% in one region, about
50% in other, and is about 70% in another region, underlining the frustrated nature of
the phase separation. It should be recalled that the microscopic observation of phase
separation has been provided by an earlier transmission electron study on this system
[36]. The experimental tool used for the present work has allowed us to study the sys-
tem in different length scales, thus enabling a systematic investigation on the nature of
phase separation. In conclusion, we have reported the imaging of the complex phase
separation in the newly discovered $K_xFe_{2-y}Se_2$ superconducting system by mapping
the lattice order using a nano-focus scanning x-ray diffraction. An expanded phase
with superlattice modulation is found to co-exist with a compressed phase, in a mul-
tiscale frustrated spatial distribution, having direct consequence on the non-magnetic
and magnetic properties of the system. The observed complex landscape of the phase
separation recalls the case of a superoxygenated $La_2CuO_{4+y}$ [47] in which a fractal
distribution of dopants appear to enhance the superconductivity. Indeed, the phase
separation shown in $K_xFe_{2-y}Se_2$ chalcogenides appears to be an important feature for
the understanding of the physics of superconductivity in these materials, similar to the
one discussed for the cuprates and other related systems [50-53].
Chapter 5

The Microstrain-Doping Phase Diagram of the Iron Pnictides: Heterostructures at Atomic Limit (HsAL)

The 3D phase diagram of iron pnictides where the critical temperature depends on charge density and microstrain in the active FeAs layers is proposed. The iron pnictides superconductors are shown to be a practical realization of a heterostructure at the atomic limit made of a superlattice of FeAs layers intercalated by spacer layers. We have focussed our interest on the $A_{1-x}B_xFe_2As_2$ (122) families and we show that FeAs layers have a tensile microstrain due to the misfit strain between the active layers and the spacers. We have identified the critical range of doping and microstrain where the critical temperature gets amplified to its maximum value.  

5.1 Introduction

Understanding the quantum mechanism that allows for a macroscopic quantum condensate, a superfluid or a superconductor, to resist the decoherence effects of high temperature is a major topic in condensed matter, quantum computing and in the search for quantum mechanisms in the living cell. The evidence that it is possible to achieve a quantum condensate of fermions at high temperatures is provided by the so called high \( T_c \) superconductors. Recently the discovery of the new FeAs high \( T_c \) superconducting multilayers has provided a test for the reliability of the models already proposed to explain high \( T_c \) superconductivity (HTcS) in other complex materials. The structure of the iron pnictides superconductors is made of a superlattice of \([FeAs]_\infty^{Q+\delta} \) with \( Q = 1 \), layers intercalated by spacers (oxide layers like \([LnF_{y}O_{1-y}]_\infty^{Q-\delta} \) or \([LnO_{1-y}]_\infty^{Q-\delta} \) in the “1111” family or metallic atomic layers \([(A^{x}_{1-x}B^{\pm 1}_x)^{1/2}]_\infty^{Q-\delta} \) in the “122” family); therefore they represent practical realizations of a heterostructure at the atomic limit (HsAL), which was described to be the essential material architecture for the emergence of HTcS [2]. In fact, different realizations of HsAL are the cuprate superconductors, where the \([CuO_2]_\infty^{2+\delta} \) active layers are intercalated by spacers like the \([La_{2}O_{2+y}]_\infty^{2-\delta} \) block layers, and magnesium diborides, where the \([B_{2}]_\infty^{-3+\delta} \) active layers are intercalated by spacers like \([Al_{1-x}Mg_{x}]_\infty^{3-\delta} \) layers [54, 55]. Experimental results on pnictides have shown that the chemical potential should be driven into a particular point of the electronic phase diagram by controlling the charge density [1], the pressure, and the spacer material in order to reach the superconducting phase with \( T_c \) as high as 55 K. Therefore it now well established that all known HTcS superconductors have the HsAL material architecture. In these superlattices the metallic active layers have strong covalent bonds (the \( CuO_2 \) layers, the graphene-like \( B_2 \) monolayers, or the molecular FeAs4/4 layers) intercalated by spacers made of different materials with a different electronic structure (fcc rocksalt oxide layers like \( La_{2-x}Sr_xO_{2+y} \) [3, 4], or hcp metallic Mg/Al layers [54, 55], and rare earth oxide layers or atomic metallic layers pnictides “1111” or “122” family, respectively).
5.2 Manganites HsAL

The same kind of architecture is also observed in manganite perovskites $AMnO_3$ that show colossal magnetoresistance (CMR). The perovskites are composite materials made of transition metal oxides and rare earth oxides AO. This structure is formed by the matching of the equilibrium (A–O) distance in the rare earth metal oxide and the equilibrium (M–O) bond length in the transition metal (M = Mn) oxide. Ideal matching occurs where $t = (A − O)/((M − O)\sqrt{2})$, the geometric tolerance factor, is unity. Also these materials can be considered HSAL, made of a superlattice of $[MnO_2]_{\infty}^{-2}$ bcc layers intercalated by spacers of $[LnO]_{\infty}^{-2}$ rare earth oxide fcc layers. The CMR phenomenon occurs at particular values of charge transfer $\delta$ (also called doping) between the active layers $[MnO_2]_{\infty}^{-2+\delta}$ and the spacer layers $[A_1^{+3}B_x^{+2}O]_{\infty}^{2-\delta}$, but also for a fixed carrier concentration $\delta$ they reveal a direct relationship between the Curie temperature and the average ionic radius of the rare earth in the spacer layers i.e. the geometric tolerance factor. In a superlattice of two different components the lattice mismatch is measured by the misfit strain, defined as $\eta = (a_1 − a_2)/<a>$ with $<a> = (a_1 + a_2)/2$, where $a_1(a_2)$ is the lattice parameter of the first (second) component when it is well separated. Assembling the two components results in a superlattice where the lattice mismatch is accommodated by a resulting compressive (tensile) microstrain in the first (second) component or vice versa. It is trivial to show that the superlattice misfit strain in the perovskites between bcc monolayers and fcc monolayers is given by $\eta = 1-t$. Therefore the CMR phenomenon occurs at particular values of doping and misfit strain. In high $T_c$ cuprate superconductors it was proposed that the maximum $T_c$ occurs in a particular point of the electronic structure of the HsAL, where the chemical potential is tuned to a particular point changing the lattice parameters and/or the charge density in the active layers to get a shape resonance (called also Feshbach resonance) of the interband pairing in a multiband superconductor [56].
5.3 Cuprate HsAL

The microstrain in the active metallic layers has been proposed to be the conformational parameter or the physical variable for a HsAL that describes the tuning of the chemical potential to the Feshbach resonance by lattice variations [11, 12], i.e., by changing the chemical pressure or internal pressure. For doped \(La_{2-x}Sr_xO_{2+y}\) (La214) cuprate superconductors, where the \([CuO_2]^{\infty}_{\infty}\) active layers are intercalated by spacers \([La_{2-x}Sr_xO_{2+y}]^{\infty}_{\infty}\), it is easy to calculate the tolerance factor, and to deduce the misfit strain, showing that the copper oxide active layers are under a compressive chemical pressure. However in cuprates it was not possible to calculate the tolerance factor and the misfit strain in other families because of the intricate structure of block layers with a plurality of cations having largely different coordination numbers. The information on the elastic field acting on the active layers in the strained layers of a superlattice can be obtained by measuring the microstrain [57-59]. This is given by the difference of the measured lattice parameter of the first component in the assembled compound and the lattice parameter of the first component when it is isolated. This problem was in fact solved for the cuprates by measuring the compressive microstrain of the \(CuO_2\) monolayer \(\varepsilon = -(r - R_0)/R_0\), where \(r\) is the measured average Cu–O distance in the superlattice and \(R_0 = 0.197\) nm is the Cu–O equilibrium distance in the well separated \([CuO_2]^{\infty}_{\infty}\) layers. In the strained superlattice the tensile microstrain in the spacer layers is expected to have the same absolute value as the compressive microstrain in the active layers. In the case of similar elastic constants in the two components the misfit strain (measuring the internal chemical pressure) is twice the microstrain. Therefore it was possible to put in the same phase diagram all families of cuprates where the elastic field due to the lattice mismatch is measured by microstrain and the charge density in the active layers by doping [57-59]. In these 3D phase diagrams there are regions of charge ordering, regions of phase separation, critical points and finally regions of HTcS. It was proposed that the highest \(T_c\) occurs at a critical point in the 3D phase diagram where the phase separation vanishes. Recently a model has been pointed out that shows that, if there is a multiband metal in the active layers in a range of values of doping and microstrain, then the system shows phase...
separation and there are critical points where the phase separation vanishes. A similar phase diagram has been proposed for diborides [60]. The purpose of this work is to show that also for the new iron pnictides both the microstrain and the charge density in the $[\text{FeAs}]_\infty^{Q+\delta}$ layers are essential parameters for driving the chemical potential to a particular point with optimum doping and microstrain. We have focused our interest on the “122” family where the spacer layers are simple metallic atomic layers. In the undoped superlattices the active layers $[\text{FeAs}]_\infty^{-1}$ and $[\text{FeAs}]_\infty^{-0.5}$ increasing the ionic radius in the spacer suffer a tensile microstrain. The FeAs equilibrium distance in the $[\text{FeAs}]_\infty^{-1}$ is 8.2 pm longer than in $[\text{FeAs}]_\infty^{-0.5}$ superlattices; therefore the lattice of the FeAs layers show a large lattice relaxation with the variation of the formal chemical charge. From these data we can deduce the microstrain as a function of doping and we have identified the critical values of microstrain and doping where the maximum $T_c$ occurs in the “122” iron pnictides families”.

5.4 Microstrain-Doping Phase Diagram for Pnicitides HsAL

In Figure 5.1 the Fe-Fe distance is plotted as a function of the average ionic radius in the spacer layers for the “122” family of FeAs based pnictides. The systems where intercalated ions in the spacer layers have the same charge are connected by a polynomial line. It is worth to notice that the two curves linking the systems with intercalated $A^+$ ions and $A^{2+}$ ions are approximately parallel. We remark that there is a non-linear response of the lattice as a function of the ionic radius, if it is too small (like that of lithium), i.e. below a critical radius of the ions in the spacers, it does not introduce a microstrain in the FeAs layer, therefore we take the value of the Fe-Fe distance in this regime as the unstrained distances are $R_0^{-1} = 276.35$ pm and $R_0^{-0.5} = 268.05$ pm in the $[\text{FeAs}]_\infty^{-1}$ and $[\text{FeAs}]_\infty^{-0.5}$ layers respectively. The microstrain of the $[\text{FeAs}]_\infty^{-1}$ layers can be easily measured. In fact, these layers are made of edge sharing $\text{FeAs}_4$ tetrahedral units where the FeAs bond length remains constant and therefore the chemical mismatch pressure, the misfit strain, induces only a rotation of the bonds pushing the
Figure 5.1: The Fe–Fe distance is plotted as a function of the average ionic radius for the 122 family of FeAs compounds [24, 25]. Ions with the same charge are arranged along the same curve. It is worth to notice that the curves referred as $A^+\,$ ions and $A^{2+}\,$ ions are approximately parallel. In fact, for systems with charge + 1 on the FeAs layers, the FeAs equilibrium distance is 8.3 pm bigger than FeAs equilibrium distance for systems with charge + 0.5 on the FeAs layers. Above a critical ionic radius the distance between the curves is 8.3 pm, and this value is constantly increasing the ionic radius.
Figure 5.2: The Fe–Fe distance is plotted as a function of the FeAs layer charge for the 122 family in FeAs compounds. The bold line indicates the variation of the FeAs bond equilibrium distance as a function of the charge in the layer.
As-Fe-As bond out of the ideal value of the tetrahedral angle 109.28°, where the ideal lattice parameter of the orthorhombic lattice is \(a_o = \sqrt{2} a_T = 552.7\) pm. The microstrain is therefore given by \(\varepsilon = (a_o/552.7 - 1) = (a_T/390.82 - 1)\).

The figure shows that there is lattice contraction of 8.3 pm (with a constant ionic radius in the intercalated layers). In Figure 5.1 the curves of doped iron pnictides with \([(Ba^{+2}_{1-x}K^{+1})1/2]_{\infty}^{+1-\delta}, [(Sr^{+2}_{1-x}Cs^{1})1/2]_{inity}^{+1-\delta}\) and \([(Sr^{+2}_{1-x}K^{+1})1/2]_{\infty}^{+1-\delta}\) intercalated atomic layers follow a linear line as expected for the Vegard law connecting the stoichiometric compounds. The case of spacer layers \([(Ba^{+2}_{1-x}K^{+1})1/2]_{\infty}^{+1-\delta}\) is of particular interest since the average ionic radius remains nearly constant. In Figure 5.2 we have plotted the Fe-Fe distance as a function of the charge density in the FeAs layers. Decreasing the charge in the FeAs layers, we observe a decreasing of the Fe-Fe distance as we substitute \(A^{+1}\) for \(A^{+2}\) ions. A mesoscopic phase separation is observed in the range \(0 < \delta < 0.1\) and the highest \(T_c\) is reached in the range \(0.1 < \delta < 0.2\), where we have a subtle tuning between the charge density and elastic strain field which are non-trivially mixed. The variation of the unstrained Fe-Fe distance, only due to the variation of the formal charge \(\delta\) in the FeAs layers, is indicated by the solid line \(R_0(\delta) = 276.35 - 16.6\delta\) pm The microstrain is a response function of the material which measures the accommodated misfit strain between spacer and active layers. The microstrain in the active layers, defined as \(\varepsilon = (R(\delta) - R_0(\delta))/R_0(\delta)\), where \(R(\delta)\) is the measured Fe-Fe distance in the doped superlattice, is plotted in Figure 5.3 as a function of the charge density (or doping). In the microstrain-doping plane we can see that there are regions of striped phase i.e. a region of itinerant magnetic order with orthorhombic lattice distortions, at doping range \(\delta = 0\), a phase separation region for \(0 < \delta < 0.2\) and the shaded area indicates the maximum \(T_c\) region centered at the critical microstrain \(\varepsilon_c \approx 0.12\), misfit strain \(\eta_c = 2\varepsilon \approx 0.24\) and doping \(\delta_c \approx 0.2\).
Figure 5.3: The microstrain is plotted as a function of the FeAs layer charge for the 122 family in FeAs compounds. The shaded area indicates the maximum $T_c$ region.
5.5 Semiconductor Heterostructures Versus Superconducting HsAL

We have shown that cuprates, diborides and pnictides have a similar heterostructure at the atomic limit. This architecture is found in all lamellar materials, exhibiting HTcS, with two repeated different layers: one which is superconducting, the other which is a spacer. The alternating layers show periodically compressive and tensile stress which is measured and named microstrain. A couple of compressive and tensile alternated layers is a typical feature of a specific kind of semiconductor heterostructures named strain-balanced structures. These are pseudomorphic superlattice structures made of alternated tensile and compressive strained layer. Because of the stress balancing, the tensile/compressive coupled layers reach the in-plane lattice parameter $a_m$. In order to achieve the overall zero-stress condition the alternating layer stack should be grown on a substrate with the same lattice parameter. The presence of a periodically alternated compressive/tensile strain in the superconducting/spacers multilayer develops to balance the stress acting on the stack, as happens in semiconducting strained-balanced superlattices. In an infinite superconducting crystal the presence of a residual stress would unlimitedly increase the total amount of elastic energy stored in the crystal, leading to a nonphysical situation. Chemical pressure due to the material epitaxial growth or the hydrostatic pressure are different kinds of pressure that do not concern the model which we here discuss. An hydrostatic pressure variable besides doping has yet been used to describe the phase diagram of the Fe-based superconductor.

5.6 Conclusions

Several models have been proposed in the past in order to universally describe the phenomenon of superconductivity with a high critical temperature. We have shown that both the microstrain and the charge density on FeAs layers are essential parameters for understanding the variation of the critical temperature in the FeAs compounds (122). We propose that the presence of a periodically alternated compressive/tensile strain in the superconducting/spacers multilayer could balance the stress acting on the stack, as
happens in semiconducting strain-balanced superlattices. The critical temperature $T_c$ is controlled by both charge density and lattice effects and the maximum $T_c$ region is centered at the critical microstrain $\varepsilon_c \approx 0.12$, misfit strain $\eta_c = 2\varepsilon \approx 0.24$ and doping $\delta_c \approx 0.2$. Furthermore we have shown a large variation of the Fe-Fe distance, only due to changes of the formal chemical charge at fixed elastic strain field. In fact it is shown that the Fe-Fe distance is 8.3 pm longer for FeAs layers with formal charge $Q = -1$ than in layers with formal charge $Q = -0.5$. 
Chapter 6

Material design: On the possibility of a new multiband heterostructure at the atomic limit made of alternate $CuO_2$ and FeAs superconducting layers

We provide the material design of a possible high temperature multiband superconductor (HTMS) made of a ‘heterostructure at the atomic limit’ formed by alternate layers of electron doped FeAs and $CuO_2$ separated by intercalated NdO spacers. This new class of materials is derived from the two well known electron doped superconductors $Nd_2CuO_4$ and NdOFeAs belonging to the cuprate and the pnictide families, respectively. The calculated local electronic density of states show that both the Cu and Fe bands cross the Fermi surface. This will provide (i) superconducting Fermi arcs made by charges from the $CuO_2$ plane, and (ii) tubular Fermi surfaces, as in pnictides, by itinerant charges from the Fe atomic layer. The electronic properties of this new class of materials are presented to highlight the possibility of material design of a HTMS tuned at a shape resonance in the energy gap parameters belonging to the class of Fano-Feshbach resonances called superstripes. The Nd $L_3$ -edge x-ray absorption near edge structure (XANES) of the proposed model system is calculated and compared with the
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Figure 6.1: Crystal structure of NdOFeAs (left) and Nd$_2$CuO$_4$ (right). Superconducting Fe (in NdOFeAs) and CuO$_2$ (in Nd$_2$CuO$_4$) layers are intercalated by the same NdO fluorite spacer layers.

XANES spectra of the Nd$_2$CuO$_4$ and NdOFeAs parent compounds.  

6.1 Introduction

The recent discovery of high temperature multiband superconductivity (HTMS) in iron based compounds has provided additional support for proposals focusing on exchange-like interband paring as the driving mechanism for high temperature superconductivity. In fact the new superconducting iron-pnictide materials show four key features predicted by these models: (i) they are made of multilayers, (ii) they are multiband metals, (iii) the Fermi level of these systems is near an ‘electronic topological transition’ (ETT) and (iv) they are multigap superconductors. Following these proposals, called

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1 A. Ricci, et al., ‘On the possibility of a new multiband heterostructure at the atomic limit made of alternate CuO$_2$ and FeAs superconducting layers’ Superconductor Science and Technology 23, 052003+ (2010), ISSN 0953-2048, URL http://dx.doi.org/10.1088/0953-2048/23/5/052003
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the ‘superstripes scenario’, amplification of the superconducting critical temperature $T_c$ occurs in systems with a material architecture made of ‘metallic heterostructures at the atomic limit’ [61]. These are superlattices of superconducting units (layers, or stripes, or wires, or spheres or balls) separated by an intercalated material [62]. The electronic structure of such a system is made of multiple bands crossing the Fermi level with different symmetry and with projected partial density of states (PDOS) in different spatial locations of the heterostructure. The chemical potential appears to be tuned (by changing the structure or the charge density) in the proximity of an ETT where one of the Fermi surfaces changes its topology and/or dimensionality. Finally in this regime a key term is the exchange-like term, called interband pairing, i.e. the exchange of pairs between condensates with different order parameters in bands with different symmetries and localization. This term controls the quantum interference between different pairing channels and could be the driving force for a shape resonance or Feshbach resonance that pushes up the critical temperature. However, this regime is difficult to realize since the system near an ETT is on the verge of a catastrophe due to first order transitions triggered by impurities and disorder. Therefore in all known HTMS the shape resonance near the ETT shows up with a complex heterogeneity due to frustrated or complex phase separation. According to one of the many proposals, high $T_c$ superconductivity by the amplification of the critical temperature has been associated mainly with a material architecture consisting of a ‘heterostructure at the atomic limit’ and tuning of the chemical potential by changing the lattice or the charge density [61]. In this proposal the essential point for high $T_c$ superconductivity is not the proximity to a Mott insulator, but the material architecture that is postulated to be an intrinsic feature. The discovery of superconducting diborides in 2001 provided the first support for this model. In fact the diboride systems share a similar ‘heterostructure at the atomic limit’ with cuprates; a superlattice of quantum wells, where the superconducting atomic boron layers replace the quite different superconducting CuO$_2$ layers, and the metallic Mg spacers replace the complex spacers in the cuprates. The discovery of superconducting pnictides in 2008 [1] has provided further strong supporting for this proposal. In fact pnictides have a very similar ‘heterostructure at the atomic limit’ architecture to cuprates; a superlattice of quantum wells, where the superconducting
atomic FeAs layers replace the quite different superconducting $CuO_2$ layers and the REO (RE = rare-earth) spacers in 1111 families replace the complex spacers in the cuprates.

## 6.2 Structural model

The remarkable structural similarity of the cuprates and pnictides, from the functional point of view, can be easily visualized by considering the examples of NdOFeAs and $Nd_2CuO_4$ structures (figure 1). Both NdOFeAs and $Nd_2CuO_4$ have tetragonal symmetry at room temperature with similar lattice parameters. The NdO spacer layer is identical in both systems (Figure 6.1). While the superconducting FeAs layers with reversed fluorite structure appear to be quite different from bcc $CuO_2$ layers, from the point of view of electronic transport, these two have identical roles to play. The ‘heterostructures at the atomic limit’ are characterized, first, by charge transfer between the superconducting layers and the spacers and, second, by the superlattice misfit strain. The NdOFeAs and $Nd_2CuO_4$ are kinds of model systems where the superlattice misfit strain seems to play an important role in the superconducting properties. Both these systems become superconductors by charge transfer of electrons from the spacer to the superconducting layers. In both systems the NdO fluorite layers are under a compressive microstrain due to the superlattice misfit strain. Also in both, the superconducting planes, Fe and $CuO_2$ in the pnictide and cuprate systems, respectively, are under a tensile microstrain that favors electron doping. The compressive microstrain in the NdO fluorite layers allows the formation of oxygen ion vacancies that can also provide electronic charge transfer to the superconducting plane in the fluorite spacer layer. Both systems show interesting magnetic phase transitions. However, unlike NdOFeAs, $Nd_2CuO_4$ shows no structural phase transition and continues to be in the tetragonal phase even at low temperature, which is also found to be true for the doped compounds ($Nd_{1.85}Ce_{0.15}CuO_4$, and $Nd_{1.85}Ce_{0.15}CuO_{3.965}$) [31].

In this work we propose a possible new class of materials made of composite heterostructures where both $CuO_2$ and FeAs layers are embedded in the same superlattice. Figure 6.2 provides the model crystal structure of such a system, $Nd_4CuO_6Fe_2As_2$. 

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Figure 6.2: Structure of the $Nd_4CuO_6Fe_2As_2$ system formed by combination of $CuO_2$ and FeAs layer units intercalated by NdO fluorite layers.
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<table>
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</tr>
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<tr>
<td>As</td>
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<td>0</td>
<td>0.30</td>
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Table 6.1: Crystallographic parameters of the Nd$_4$CuO$_6$Fe$_2$As$_2$ system formed by combination of CuO$_2$, and FeAs layer units intercalated by NdO fluorite layers. Space group: I4/mmm, $a = b = 3.96\,\text{Å}$, $c = 21\,\text{Å}$. Crystallographic data corresponding to NdOFeAs and Nd$_2$CuO$_4$ are given in [63, 64]. As can be seen, the crystallographic structure of the new compound is similar to the parent compounds, which is expected due to the striking structural similarity between the two systems (Figure 6.1).

Table 1 presents the crystallographic details of this structure. The NdO spacer layer in this new superlattice structure separates two different kinds of charge-carrier layer either side. This implies that from the electronic structure point of view, the Nd atoms are going to have two distinct sites (electronically, two distinct PDOS for a Nd atom depending on its site). This new class of ‘heterostructures at the atomic limit’ could provide a very exciting HTMS made of CuO$_2$ and FeAs superconducting layers with different superconducting gaps in the different layers and a single superconducting critical temperature controlled by proximity effects, i.e. the interband exchange-like pairing interaction.

6.3 DOS calculations

The PDOS of the constituent elements of the Nd$_4$CuO$_6$Fe$_2$As$_2$ system is shown in figure 3. The PDOS calculation method is described in a recent article [34]. As expected from the Nd$_2$CuO$_4$ and NdOFeAs electronic structure, the near Fermi level ($E_F$) states in this case are also dominated by the d states of Cu and Fe. Importantly, as is evident from the Nd PDOS (upper two panels in Figure 6.3), there is a relatively large weight for the Nd f states near the $E_F$ for the two distinct Nd sites, albeit with a noticeable difference in the spectral weight distribution. The Nd ground state is [
Figure 6.3: The site projected density of states (PDOS) of the $Nd_4CuO_6Fe_2As_2$. Legends show the color code used for the different orbitals. The vertical dotted line indicate the position of $E_F$. 
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Xe]4f46s$_2$ with a partially filled 4f state. The d state also make a non-negligible contribution to the near $E_F$ DOS, especially the unoccupied states close to $E_F$. From Figure 6.1 it is evident that the major contribution to the near $E_F$ DOS comes from Nd, Cu and Fe. The calculated PDOS shows that both Cu and Fe bands cross the Fermi surface. This will provide, first, superconducting Fermi arcs made by charges from the CuO$_2$ plane and, second, tubular Fermi surfaces like in the pnictides made by itinerant charges in Fe atomic layer. It is interesting to compare how the electronic structure of these elements in the superstructure (Nd$_4$CuO$_6$Fe$_2$As$_2$) varies from that of the ‘parent compounds (NdOFeAs and Nd$_2$CuO$_4$)’. For that purpose, in Figure 6.4, we plot the PDOS of these elements in the ‘superstructure’ and ‘parent compounds’.

The d states of Cu and Fe are the key players in the quasi-particle formation of the cuprate and pnictide systems, respectively. A comparison of these d states in the ‘parent phase’ with that of the superstructure reveals substantial changes in its near $E_F$ spectral weights (Figure 6.4). From the structural point of view, the origins of such differences are not so evident. Looking back at the structure (Figure 6.1 and Figure 6.2), from the Fe site, the Fe-As charge-carrier layer in NdOFeAs and Nd$_4$CuO$_6$Fe$_2$As$_2$ have identical spacer layers (NdO) on both sides. The situation for the other charge-carrier layer, Cu-O, is similar. While these charge-carrier layers in the superstructure have identical near-neighbor environment as the parent compounds, the common spacer layer in the superstructure (NdO), sees completely different layers on both sides. This gives rise to two inequivalent sites for Nd, resulting in two different PDOS (denoted as Nd (site1) and Nd (site2) in Figure 6.3). The changes seen in the PDOS of the ‘active elements’ (Cu and Fe), especially for the d orbitals, of the superstructure in comparison with the ‘parent phase’ clearly reveals that the properties of the former are not going to be a simple superposition of the properties of the constituent parent phases. This clearly underlines the importance of the practical realization of such a system. It should be mentioned that in an experimental realization of such a superstructure, it is very probable that the structural parameters could also be modified slightly, leading to changes in the electronic structure. Alternatively, there could also be slight changes occurring in the structure due to changes in the electronic bands as a result of proximity effects. In an interesting resonant x-ray spectroscopy study on the interface between
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Figure 6.4: Comparison of the PDOS of Nd$_4$CuO$_6$Fe$_2$As$_2$ with its parent phase compounds NdOFeAs and Nd$_2$CuO$_4$. Upper right and lower right panels compare, respectively, the Fe PDOS and the Nd PDOS of the NdOFeAs and Nd$_4$CuO$_6$Fe$_2$As$_2$ systems. Upper left and lower left panels compare, respectively, the Cu PDOS and the Nd PDOS of the Nd$_2$CuO$_4$ and Nd$_4$CuO$_6$Fe$_2$As$_2$ systems. The dotted line in all panels indicates the position of $E_F$. 
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Figure 6.5: Comparison of Nd $L_3$ XANES spectra from Nd$_2$CuO$_4$ and NdOFeAs. Experimental data are shown in the right panel and the corresponding FEFF calculation results are shown in the left panel. The inset shows zoomed view of the near-edge features.

high temperature superconducting $(Y,Ca)Ba_2Cu_3O_7$ and metallic $La_{0.67}Ca_{0.33}MnO_3$, Chakhalian et al, showed the importance of orbital reconstruction and covalent bonding in designing of oxide heterostructures with engineered physical properties [65]. It is found that a charge of about -0.2 electron is transferred from Mn to Cu ions across the interface, resulting in a major reconstruction of the orbital occupation and orbital symmetry of the CuO$_2$ layers. In the present case, although the active layers, CuO and FeAs, are separated by the identical NdO spacer layer, a coupling between the active layers, especially when the spacer layer is in the doped condition, can have non-trivial consequences for the functional properties of the system.
6.4 XANES calculations

Having calculated the electronic structure, it is tempting to make use of the above in performing possible comparisons with available experimental data. Comparison with the x-ray absorption data is one way to do that. This also helps in further clarifying the electronic and structural correlations. We have used the Nd $L_3$-edge XANES data for this purpose. In Figure 6.5, we present the normalized experimental and calculated XANES spectra of the NdOFeAs and $Nd_2CuO_4$ systems. The experimental data for the $Nd_2CuO_4$ are taken from [66] while those for NdOFeAs are taken from [67]. Both the spectra show an intense peak, the characteristic white line (WL) of $Nd^{3+}$. It is worth recalling that the $L_3$ absorption process is a $2p_{3/2} \rightarrow 5\epsilon d$ (or $2p_{3/2} \rightarrow 6\epsilon s$) transition governed by the dipole selection rules ($l = \pm 1$) and hence empty states with $d$ or $s$ symmetries (and admixed states) can be reached in the final state. Since the probability for a $2p_{3/2} \rightarrow 6\epsilon s$ transition is about two orders of magnitude lower than for a $2p_{3/2} \rightarrow 5\epsilon d$ transition, the earlier can be ignored for describing the $L_3$ WL. The one-electron picture (i.e. all the orbitals not directly involved in the absorption process are passive in the final state) works well for the $L_3$ WL unless the materials of interest are mixed valence systems. In the present case, the WL appears to be typical of $Nd^{3+}$ and hence the one-electron picture could be fairly used to describe the spectra. In addition to the intense WL, other predominant near-edge features observed are a weak structure around 15 eV above the WL (feature B), and the continuum resonances appearing as a two peak structure (feature C). Interestingly, the 1111- pnictide systems show a systematic variation of the energy difference between the WL and the continuum resonance features in accordance with the REO and REA distances [40]. The slight shift in the continuum resonance peak towards the lower energy in the case of $Nd_2CuO_4$ is consistent with the slightly increased distance of the NdO bond length in this case. These results are in line with the $\Delta E \propto 1/d^2$ rule for multiple scattering resonances [41]. The XANES simulations over the $Nd - L_3$ edge were performed using self-consistent real-space multiple scattering calculations using the FEFF8.2 code [42, 43] within the muffin-tin approximation. The atomic potential is calculated self-consistently using a cluster of radius 8.0 Å. For the calculations, the energy and position dependent
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6.5 Results and Discussions

The XANES calculations show overall agreement with the experimental data for both the NdOFeAs and $Nd_2CuO_4$ systems (Figure 6.5). However, a detailed comparison (inset Figure 6.5) indicates a difference in the amplitudes of the different near-edge features of $Nd_2CuO_4$ upon compression. A 3% compression of the $Nd_2CuO_4$ gives reasonable matching of the near-edge features of this with that of NdOFeAs.

Hedin-Lundqvist optical potential [44] has been selected as the exchange-correlation potential. The total electronic potential was constructed by spherically averaging the muffin-tin potentials on each atom and keeping constant the potential in the interstitial region between the muffin-tin spheres. The f states of the Nd were kept frozen to achieve convergence of the self-consistent potential.
features, especially the feature B. It should be recalled that a similar feature B has been detected in the $L_3$-edge XANES spectra of different cuprate compounds, but discussion of this feature in the past was limited to the structural symmetries [66]. With the appearance of iron-pnictide superconductors, such a feature in the rare-earth $L_3$-XANES spectra again come to light. In the REOFeAs system, it is observed that feature B changes systematically with the rare-earth size [67]. Comparison with multiple scattering calculations and the experimental data revealed that feature B has both a local structural and an electronic origin [68]. As discussed earlier, although the NdOFeAs and $Nd_2CuO_4$ share identical crystal configurations, with similar layer structures (Figure 6.1), a good overlap of the XANES features is not seen in either the experimental or theoretical calculations (Figure 6.5). In order to check the possible role of the difference in the lattice constants of the two systems in the above, we have studied the effect of compression of the $Nd_2CuO_4$ unit-cell on its XANES spectrum in comparison with that of the NdOFeAs. Results of such a study are presented in figure 6.

A 3% compression of the $Nd_2CuO_4$ unit-cell gives reasonable matching of the near-edge XANES features of this with that of NdOFeAs. Looking at the evolution of the near-edge features (Figure 6.6 left panel), it is evident that feature B is also influenced by the unit-cell compression. The continuum resonance peaks also show the expected shift towards higher energy with the shorter unit-cell following the $\Delta E \propto 1/d^2$ empirical rule [67]. In fact, such a small change in the lattice constants of the $Nd_2CuO_4$ was actually implemented in generating the superstructure shown in Figure 6.2. This small but finite difference in the lattice constants of the two parent phases involved in the superstructure is a key ingredient for handling the misfit strain in such a system. In addition, it also make the ‘superstripes scenario’ all the more interesting in such superstructures.

At this stage, it is also interesting to look into the Nd $L_3$-XANES spectrum of the $Nd_4CuO_6Fe_2As_2$ system. The FEFF calculation results for the Nd $L_3$-XANES spectra from the two Nd sites in $Nd_4CuO_6Fe_2As_2$ are shown in Figure 6.7. As expected, the spectra from the two sites show different nearedge features. There is also a substantial difference in the WL intensities of the two components. From the experimental
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Figure 6.7: FEFF calculation results for the Nd L 3 XANES spectra from the two Nd sites in $Nd_4CuO_6Fe_2As_2$.
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point of view, the Nd $L_3$ -XANES spectrum of the $Nd_4CuO_6Fe_2As_2$ system should be similar to the average of the calculated spectra from the two Nd sites. A comparison of XANES spectra calculated for the NdOFeAs and $Nd_2CuO_4$ (Figure 6.5) with that of the $Nd_4CuO_6Fe_2As_2$ (Figure 6.7) shows that the latter has an entirely different near-edge structure, once again underlining the possibilities for manipulation of the electronic degrees of freedom of such superstructures, in addition to the microstrain engineering aspects.

6.6 Summary

Here we propose a novel class of heterostructures made of alternate layers of pnictides and cuprates to produce HTMS materials which have additional microscopic degrees of freedom. These HTMS are multilayers involving alternate layer components from cuprate and iron–arsenide superconductor families. In particular, we provide a specific example of a composite system involving two basic components, $Nd_2CuO_4$ and NdOFeAs. The idea of such a HTMS is motivated by the striking similarities in the structural and electronic (as evidenced by the $NdL_3$ -XANES) properties of the $Nd_2CuO_4$ and NdOFeAs systems. The electronic properties and the XANES calculations for this novel HTMS are presented to highlight the importance of such a superstructure which offers further scope for the material manipulation of high temperature superconductors.
Conclusions

The new emphasis provided by the recent discovery of iron-based superconductors have stimulated the condensed matter research community to study their common characteristics with the known cuprates and diborides. The research community is converging to the idea that the structure of these materials is a key point for the understanding of the physical mechanism that allows a quantum coherent condensate to avoid the effects of temperature decoherence. Infact all the known family of type II superconductors are superlattice formed by an active layer alternated by another that has the role of spacer. The understanding of the scenario that describe the high-temperature superconductors is of relevant importance for a new starting field that try to list their general features in order to design superconductor materials from ab initio considerations. In this thesis I have focused my attention to the study of structural properties and the critical phenomena that characterize the structure of iron-based superconductors: the iron-pnictides and the iron-chalcogenides. In the first part I have studied the tetragonal to orthorhombic structural phase transition (SPT) in 1111-pnictides that appear to be different considering polycrystalline and single crystal sample. Comparing the polycrystalline and the single crystal 1111 samples, the critical exponents of the SPT are found to be the same while the correlation length critical exponents are found to be very different. These results imply that the lattice fluctuations in 1111 systems change in samples with different surface to volume ratio that is assigned to the relieve of the temperature-dependent superlattice misfit strain between active iron layers and the spacer layers in 1111 systems. The change of the rare-earth atoms, with different atomic radius, induces a change of the elastic misfit strain between the superconducting Fe layers and the intercalated layers, that as been ob-
Conclusions

served in a changing in the SPT critical exponents. This is a common behaviour also in cuprates, and diborides. During the last year a new family of iron-based superconductors, the iron-chalcogenides, has been discovered. These systems are made of iron chalcogenide FeSe molecular layers, intercalated by A=K, Cs, Rb, Tl, (Tl,Rb), (Tl,K) spacer layers, providing the more recent practical realization of metal heterostructures at atomic limit, as cuprates and pnictides high temperature superconductors. These $A_xFe_{2-y}Se_2$ chalcogenide superconductors show both high temperature superconductivity and magnetism. In these compounds, one may tune the interplay of superconductivity and magnetism by changing the Fe-vacancy order and the superlattice misfit strain. In the second part of this work I reported the scanning X-ray nano-diffraction measurements on a single crystal of $K_{0.8}Fe_{1.6}Se_2$. Using advanced synchrotron radiation focusing down to a size of 300 nm has been possible to visualize nanoscale phase separation and to understand the complex electronic behaviour of potassium iron-chalcogenide superconductors. Starting from 600K and decreasing the temperature an intrinsic phase separation in $K_{0.8}Fe_{1.6}Se_2$ single crystals has been found at $T < 520$ K. The space resolved imaging of the phase separation permitted us to provide a direct evidence of nano phase domains smaller than 300 nm and different micron size regions with percolating magnetic or non-magnetic domains forming a multiscale complex network of the two phases. The phase separation appears on multiple scales from micron-scale to nano-scale like in cuprates, diborides and pnictides. Several theories have described the complex phase separation as an intrinsic feature of all known high-Temperature superconductors. In the last part of the thesis I have shown a possible idea of new superconductor by material design. The multi-layer architecture, a common feature of cuprates, diborides, pnictides and chalcogenides, underlines the relevance of lattice effects for high-temperature superconductivity. The structure of the iron-based superconductors is made of a superlattice of active layers intercalated by spacers and therefore they represent practical realizations of a ‘heterostructure at the atomic limit’ (HsAL) that was described to be the essential material architecture for the emergence of high-Temperature superconductivity. Infact, we propose a novel class of heterostructures made of alternate layers of pnictides and cuprates to produce an High-Temperature Multiband Superconductor (HTMS) materials. These HTMS
are multilayers involving alternate layer components from cuprate and iron-arsenide superconductor families. In particular, we provide a specific example of a composite system involving two basic components, \(Nd_2CuO_4\) and NdOFeAs. The idea of such a HTMS is motivated by the striking similarities in the structural and electronic (as evidenced by the Nd \(L_3\)-XANES) properties of the \(Nd_2CuO_4\) and NdOFeAs systems. The electronic properties and the XANES calculations for this novel HTMS are presented to highlight the importance of such a superstructure which offers further scope for the material manipulation and design of high temperature superconductors.
List of Publications

List of Original Papers


3. A. Ricci, et al., “Nanoscale phase separation in the iron chalcogenide superconductor \(K_{0.8}Fe_{1.6}Se_2\) as seen via scanning nanofocused x-ray diffraction” Physical Review B 84, 060511+ (2011),

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