

MATERIALS, PROPERTIES, AND MECHANISMS IRON-BASED SUPERCONDUCTORS

edited by Nan-Lin Wang Hideo Hosono Pengcheng Dai

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CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742

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International Standard Book Number-13: 978-9-81430-323-1 (eBook - PDF)

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Preface

Superconductivity has just celebrated its 100th birthday, and yet despite its advanced age, it has continued to be a field of active research. Much of this is due to continued discovery of new materials and new phenomena. Heike Kamerlingh Onnes won the Nobel Prize for his discovery of superconductivity in mercury, and coined the word "superconductivity." However, the microscopic origin of superconductivity had not been understood until the discovery of Bardeen-Cooper-Schrieffer (BCS) theory in 1957. The BCS theory is based on Landau's Fermi liquid for metals, and stipulates that superconductivity occurs because electrons in the superconducting state form Cooper pairs through the electron-phonon interactions to overcome the Coulomb repulsive force. The superconductors that can be described within the BCS theory are called conventional or BCS superconductors. In 1986, a new family of superconductors with high critical temperature (high- T_c) based on copper-oxides was discovered by Johannes Bednorz and Karl Müller, opening a new era of superconductivity. Instead of being metallic, the undoped parent compounds of copper oxide superconductors are Mott insulators, and it is generally believed that superconductivity in these materials is different from the BCS mechanism. For this reason, these materials are called unconventional superconductors. However, in spite of more than 25 years of intensive work, there is still no consensus on the microscopic origin of superconductivity in the copper oxides. In early 2008, another family of unconventional superconductors iron-based superconductors — was discovered by Hosono's group. This discovery immediately caused great excitement in the community because this is only the second class of high-T_c superconductors in addition to the copper oxides. Since the original discovery paper four years ago, more than 4000 papers have been published

on the subject. Although it is generally agreed that superconductivity in both iron- and copper-based superconductors originates from electron-forming Cooper pairs in the superconducting state, much is under debate concerning the microscopic origins for the pairing interaction. In this book, we summarize the recent progress in the field and highlight important accomplishments over the past four years.

The first two chapters focus on the materials and their characterizations. The story of how the superconductivity in Fe-pnictides was discovered is described by Hosono in the first chapter. The crystal structure and properties of parent compounds and growth of the single crystals and epitaxial thin films are also presented. The second chapter is devoted to the Fe-chalcogenide system $K_{1-x}Fe_{2-y}Se_2$, which appears to exhibit very different properties from that of Fe-pnictide compounds. Those overviews are followed by the physical properties investigations and theoretical understandings. The experimental explorations of electronic structures, Fermi surface topologies, the charge excitations at various energy scales, and superconducting gap symmetry in terms of angle-resolved photoemission, quantum oscillation, and optical spectroscopy techniques are overviewed in Chapters 3, 4, and 5, respectively. The magnetic structure and spin excitations probed by neutron scattering and nuclear magnetic resonance techniques are summarized in Chapters 6 and 7. Theoretical understanding of the charge and spin excitations, paring symmetry, and pairing mechanism based on different approaches, i.e., weak coupling versus strong coupling, are overviewed in the last three chapters. We hope that the book could serve as the primary reference for graduate students and researchers working in the field.

Iron-based superconductors are currently still under intensive research. During the period of our editing this review volume, new developments have been made in various aspects in this field. A number of review articles, special issues in several journals and a monograph on the physics of iron-based superconductors also appeared in literature. To benefit our readers, we list several of them:

Y. Izyumov and E. Kurmaev, *High-T_c Superconductors Based on FeAs Compounds*, Springer Series in Materials Science, vol. 143,

Springer-Verlag Berlin Heidelberg (2010). (This is the first monograph on the physics of iron-based superconductors.)

- 2. D.C. Johnson, The puzzle of high temperature superconductivity in layered iron pnictides and chalcogenides, *Adv. Phys.*, **59**, 803 (2010). (It is a comprehensive review covering papers up to early 2010.)
- 3. M. D. Lumsden and A. D. Christianson, Magnetism in Fe-based superconductors, *J. Phys.: Condens. Matter*, **22**, 203203 (2010).
- 4. G. R. Stewart, Superconductivity in iron compounds, *Rev. Mod. Phys.*, **83**, 1589 (2011).
- 5. R. Pottgen and D. Johrendt, 100 Years of Superconductivity, *Zeitschrift fur Kristallographie*, **226**, 309 (2011). (Superconducting materials were reviewed from crystal chemical view.)
- 6. G. Crabtree, L. Greene, and P. Johnson (edited), Celebrating 100 years of superconductivity: special issue on the iron-based superconductors, *Rep. Prog. Phys.*, **74**, 12 (2011). (This special issue consists of 13 review articles. Experimental and theoretical approaches to pairing mechanism are highlighted.)
- H. Hosono, H. Fukuyama, and H. Akai (edited), Special issue on iron-based superconductors, *Solid State Commun.*, **152**, 631–746 (2012). (This special issue consists of 18 articles. Experimental and theoretical approaches to the physical properties are highlighted.)
- 8. H. Hiramatsu, T. Katase, T. Kamiya, and H. Hosono, Thin film growth and device fabrication of iron-based superconductors, *J. Phys. Soc. Jpn.*, **81**, 011011 (2012).

Chapter 1

Iron-Based Superconductors: Discovery and Progress in Materials

Hideo Hosono

Frontier Research Center & Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8503, Japan hosono@msl.titech.ac.jp

LaFeO_{1-x} F_x with $T_c = 26$ K was reported in early 2008. Since then, more than 4,000 papers have been published and the maximum T_c reached 56 K, which is next to high- T_c cuprates. Iron-based superconductors have several unique properties mostly arising from their multi-orbital nature. The presence of a vast number of parent materials is a characteristic of this system. This chapter describes the background research to the discovery, the crystal structure and properties of parent materials, and growth of the single crystals and epitaxial thin films.

1.1 Introduction

Superconductivity is the most dramatic and clear-cut phenomenon which occurs in condensed matters and its potential impact on our society is huge toward realization of low carbon emission society. Although the theoretical framework describing superconductivity was established by the BCS theory, there is no solid theoretical guideline which is truly convincing for experimentalists in this field to approach high- T_c materials even now. These are the reasons why superconductivity has been attracted much attention of many scientists for a century since the discovery of superconductivity in Hg by Kamerlingh Onnes.

Prior to the discovery of cuprate superconductors in 1986, BCS theory seemed to fully explain superconductivity. However, Müller and Bednorz's discovery¹ led to a critical temperature (T_c) above the liquid nitrogen temperature, (e.g., $T_c = 90$ K of YBa₂Cu₃O_x),² and inevitably required a significant modification to the theory. A breakthrough discovery occurred in traditional metal-based superconductors in 2001, i.e., the finding of MgB₂ with $T_c = 40$ K by Akimitsu's group,³ which was basically explained by BCS theory.

The new iron-based superconductor $(LaFeAsO_{1-x}F_x: T_c = 26 \text{ K})$ found by Hosono's group⁴ in January 2008 rekindled intensive research in this area and opened a new frontier for superconductivity. In the early stage, this new superconductor family was called "Pnictide Superconductors". However, researchers now call them "Iron-based Superconductors" (FeSCs) because detailed measurements and evaluations have clarified that they all have similar electronic structure where the electrons derived from Fe ion play an essential role in superconductivity.

An electron has a charge and a spin. Magnetism emerges from the long-range ordering of electron spins, while superconductivity occurs on the formation of Cooper pairs of electrons, which are mostly diamagnetic due to spin singlet state (a spin triplet superconductor is rare such as $SrRuO_3^5$). Therefore, the relationship between magnetism and superconductivity had long been believed to be ambivalent, and the use of the magnetic element with a large spin moment, typically Fe, Co and Ni, was avoided in the field of superconductivity. Hence, the discovery of a high- T_c superconductor based on iron significantly impacted research in this field. Material scientists and physicists encountered a new frontier of potential elements for superconducting material exploration.

1.2 Small History on Discovery and Progress in Parent Materials

We have been concentrated on exploration of new transparent oxide conductors and semiconductors since 1993.⁶ Our study on transparent p-type semiconducting materials with high hole mobilities began with $CuAlO_2$,⁷ and led to the discovery of LaCuChO (Ch: chalcogen) with high performance.⁸ As a succession of this finding, we focused on exploration of novel magnetic semiconductors by replacing Cu⁺ with a closed 3d shell structure with magnetic elements with an open 3d shell such as Fe^{2+} or Mn^{2+} . When we began this subject. we did not target the superconductivity, but fortunately we routinely measured the resistivity of our newly prepared materials down to 2 K because another our concern was to convert a cement component 12Ca0·7Al₂O₃(C12A7) from insulating state to metallic state.^{9,10} During these experiments, simultaneous substitution of Fe^{2+} or Ni²⁺ for Cu⁺ and P³⁻ or As³⁻ for Ch²⁻, led to discover of low- T_c superconducting materials: LaFePO ($T_c = 5$ K),¹¹ LaNiPO $(T_c = 3 \text{ K})^{12}$ and LaNiAsO $(T_c = 2.4 \text{ K})^{13}$ as summarized in Fig. 1.1. The T_c values of these materials did not markedly increase by impurity doping. Although non-doped LaFeAsO did not exhibit superconductivity, it displayed anti-ferromagnetism at a Neel temperature (T_N) of ~150 K, and changed into a superconductor with $T_{\rm c} = 26$ K upon substitution of O^{2-} by F⁻, i.e., electron doping as shown in Fig. 1.2. This discovery led to the opening of the FeSCs field, which is currently a significant part of superconductivity research.

Our group of Tokyo Tech and Takahashi group of Nihon Univ had been continuing a cooperative research on LaFePO since 2007. When we discovered the relatively high T_c in LaFeAsO_{1-x}F_x in October, 2007, the target was switched from LaFePO to LaFeAsO_{1-x}F_x and we found a raise of T_c to 43 K under a pressure of ~4GPa. This temperature exceeded the T_c (40 K) of MgB₂ and is next to the high- T_c cuprates. We submitted a letter paper describing this result to *Nature* on February 26¹⁴ and started to synthesize the LuFeAsO_{1-x}F_x at the same time. It was evident that high pressure effectively works to raise the T_c in this system. We thought if La ion with the largest radius among rare earth ions could be replaced







Figure 1.2 Resistivity-temperature curves for LaFePO and LaFeAsO $_{1-x}F_x$ along with crystal structure and the sample photo.

by Lu^{3+} , a nonmagnetic rare earth ion with the smallest radius, the highest T_c would have been realized. However, this trial was totally unsuccessful. The compound LuFeAsO itself was not obtained (even to date). During this struggle, higher T_c 's were posted on a preprint server (http://arxiv.org/archive/cond-mat) by research groups in China led by X. Cheng¹⁵ or Z.-X. Zhao¹⁶ in early March. They obtained higher T_c by replacing La ion with Ce, or Sm ion with an open 4f-shell. These reports were shocking for us because we had been intentionally avoided the use of magnetic rare earth ion based on an experimental result (presented at 15th Conference on Intercalation at Korea in May, 2007^{17}) that superconductivity disappears when La ion in LaFePO ($T_c = 4$ K) was replaced by Ce.¹⁸ That is, we misunderstood without careful checking whether or not the 4f orbitals of rare earth ions are close to the Fermi level which is primarily composed of Fe 3d orbitals. According to a band calculation, the valence band width of LaFePO is $\sim 20\%$ larger than that of LaFeAsO.¹⁹ Thus, Ce 4f electron strongly interacts with the carriers in LaFePO and resulted in the conversion to heavy fermion,²⁰ while in CeFeAsO such a conversion did not occur owing to that Ce 4f level is not so close to the E_F . At the end of May, another shocking paper²¹ reporting the superconductivity in $Ba_{1-x}K_xFe_2As_2$ was posted on the cond.mat. by Dirk Johrendt's group in Germay because we had been continuing the electron-doping to $BaFe_2As_2$ after discovering a T_c (4 K) in $LaNi_2As_2$ in March.²²

Figure 1.3 summarizes the progress of Fe (Ni)-based superconducting materials at the initial stage covering the discovery of major parent materials. The abscissa denotes the date of a paper received in a journal (before 2008) or posted on the preprint-server (after 2008).

1.3 Crystal Structure of Parent Materials

Although numerous FeSCs have been reported, their parent materials may be classified into five types in terms of crystal structures (Fig. 1.4). The structural unit common to these materials is the square net of Fe²⁺ (formal charge) coordinated tetrahedrally by four pnictgen (Pn) or chalcogen (Ch) atoms. Unlike cuprate superconductors, where the parent materials are Mott insulators, this layer exhibits a metallic conductivity without doping. An insulating blocking layer composed by M, MO or MF etc., where Mindicates a metallic element such as an alkali metal, alkaline earth, or rare earth element that lies between FePn layers. The local structure of the FePn layer is affected directly by the atomic (or ionic) size of M because M elements in the blocking layer bond to Pn elements. The features of each parent material for FeSCs are described below.

1.3.1 1111-Type Materials (LnFePnO, Ln: Lanthanide)

Compounds with the same structure as LaFeAsO, the earliest versions of FeSCs is called the "1111-type" after atomic composition ratio. Figure 1.4a shows their crystal structure, which is a ZrCuSiAs-type structure with a tetragonal P4/nmm space group. Over 300 materials belong to this group, including the p-type wide-gap semiconducting LaCuChO (Ch = S, Se, Te) mentioned in Section 2. Although LaFePO and LaFeAsO along with their crystal structures were reported more than 10 years ago,²³ superconductivity was discovered in 2006¹² for the former and 2008⁴ for the latter. Their structural and electronic two-dimensionality is highest among the



Figure 1.3 Time series of papers reporting superconductivity in each parent compound of iron/nickel pnictide (chalcogenide). Date after March 2008 denotes day posted on Condensed Matter Preprint server.



Figure 1.4 Crystal structure of parent compounds. (a) 1111-type, (b) 122-type, (b') 245-type, (c) 111-type, (d) 11-type, and (e) the homologous-type. See also Color Insert.

five types of parent materials except a type with a thick block, and only this group has $T_{\rm c}$ values above 50 K.

The unit cell of 1111-type compounds ($a \sim 0.4$ nm, $c \sim 0.8$ –0.9 nm) contains two molecular formulae, and is composed of an alternating stack of positively charged LnO layers and negatively charged FeAs layers along the *c*-axis. The FeAs layer is constructed with an array of edge-shared FeAs₄ tetrahedrons constituting the planar square net of Fe. As mentioned above, the local structure of the FeAs layer is the same in each of FeSCs. The distance between the adjacent FeAs layers corresponds to the length of the *c*-axis (\sim 0.8–0.9 nm). The formal valence state of each atom is Ln³⁺, Fe²⁺, As³⁻, or O²⁻. A Fe²⁺ contains 6 electrons in five 3d orbitals and each of them participates to the Fermi level. The lanthanide elements from La to Gd can occupy the Ln site for a 1111-type of material with Pn = P²⁴, whereas Ho and Y can also occupy the Ln site for Pn = As.²⁵

AeFeAsF (Ae = Ca and Sr) with an AeF blocking layer belongs to this type.²⁶ Structural chemistry of layered d-metal pnictides oxides were reviewed in references.^{27,28}

1.3.2 122-Type Materials (AeFe₂Pn₂, Ae: Alkaline Earth or Eu)

122-type materials have a "Th Cr_2Si_2 " crystal structure with a tetragonal I4/mmm space group.²⁹ This structure can accommodate a variety of elements³⁰ like perovskites in oxide system. CeCu₂Si₂, a prototype heavy fermion superconductor, belongs to this group.

In the case of AeFe₂P₂, lanthanides (La-Pr, Eu) as well as alkaline earth elements can occupy the Ae site, while in AeFe₂As₂ the Ae site can be occupied by alkaline earth, alkali metal, and Eu²⁺. Figure 1.4b shows the crystal structure for the 122-type. The layer composed of Ae ions, which is thinner than the Ln-O layer of the 1111-type, is sandwiched by the FeAs conducting layers. The separation between the adjacent FeAs layers of the 122-type (0.5–0.6 nm) is shorter than that of the 1111-type (0.8–0.9 nm). Because the nearest FeAs layers face each other with a mirror plane, the lattice parameter *c* is twice the FeAs-FeAs distance. The lattice parameter $a(\sim 0.4 \text{ nm})$ is almost the same as that of the 1111-type. Consequently, both 1111 and 122type materials have similar Fe-Fe distance in the FeAs layer. Since large-sized single crystals of several millimeters can be obtained using Sn or FeAs as a flux, the physical properties of 122-type are well evaluated relative to other types of FeSCs. Johrendt's group was the first to report superconductivity for 122-type materials.²¹

Recently, new 122- type compounds showing relatively high T_c value, e.g., 30 K for $K_x Fe_2 Se_2^{31}$ and 27 K for $Ce_{0.8}$ (FeSe_{0.98})₂,³² have been reported. Although these materials were initially classified as the 11-type intercalated by alkali metal, they have the 122-type structure with a tetragonal I4/mmm space group. These materials contain large Fe vacancy, $\sim 1/4$ of Fe ion sites, and the composition of the parent material may be described as A_2 Fe₄Se₅ (A = K, Rb, Cs and Tl) with high Neel temperature (~ 500 K) and a band gap (0.37 eV and 0.03 eV).³³ Thus, this family of materials may be regarded as a new parent compound called "245-type" (Fig. 1.4b').

1.3.3 111-Type Materials (AFePn, A: Alkali Metal)

While *Ae* ions (formal charge of +2) exists in every two FePn molecules in the 122-type, 111-type compounds contain two *A* ions (*A*: Li⁺, Na⁺) per two FePn molecules. The crystal structure of this type is known as the "CeFeSi" type, with a tetragonal P4/nmm space group (Fig. 1.4c). This type is compatible with the structure of the 1111-type where all the oxygen atoms are removed and the Ln site is occupied by Li⁺ or Na⁺. Wang *et al.*³⁴ ($T_c = 18$ K: LiFeAs) and Tapp *et al.*³⁵ ($T_c = 18$ K: NaFeAs) first reported superconductivity for 111-type materials.

1.3.4 11-Type Materials (Fe_{1+x}Se)

The 11-type has the simplest crystal structure composed of FeCh layer, and first reported by M.K.Wu group in 2008.³⁶ The crystal structure is known as " α -PbO" type with a tetragonal P4/nmm space group (Fig. 1.4d). A typical 11-type superconductor is β -FeSe ($T_c = 8 \text{ K}$).³⁶ According to the phase diagram of Fe-Se, the β -type exists in a narrow composition region (x = 0.010-0.025 in Fe_{1+x}Se), and the stable form near room temperature is α -FeAs with a hexagonal lattice and the NiAs type structure. To obtain β -FeSe, the material is kept at 400°C for prolonged duration. Medvedov *et al.*³⁷ suggested the 11-type may exhibit a high T_c (= 37 K) under 8.9 GPa.

1.3.5 Homologous-Type Materials: $(Fe_2As_2)(Ae_{n+1}M_mO_y)$

The distance between the adjacent FePn/Ch layers shortens in the order of the 1111, 122, 111 and 11-types. The homologous types of iron pnictide oxide have a thick blocking layer composed of a quasi-perovskite structure assembled by MO_5 pyramids and Ae (see Fig. 1.4e for the homologous-type (Fe₂As₂)(Sr₄Sc₂O₆). The FeAs-FeAs distance is 1.55 nm and 2.45 nm for (Fe₂As₂)(Sr₄Sc₂O₆) and (Fe₂As₂)(Ca₆(Sc,Ti)₅O_y), respectively. Shimoyama's group systematically has been studied this type of materials.^{38–40} It is natural to expect from an analogy with cuprate that T_c would be increase with the thickness of superconducting layers. Figure 1.5 shows the variation in T_c with the inter Fe-layer separation. The highest



Figure 1.5 Correlation between T_c and iron-plane interlayer distance for various layered FeSCs.⁴⁰

 T_c attained is 43 K for (Fe₂As₂)(Ca₆(Sc,Ti)₅O_y but T_c is saturated around ~1.5 nm spacing.

Recently, Nohara *et al.*⁴¹ reported $Ca_{10}(Pt_4As_8)(Fe_{2-x}Pt_xAs_2)_5$ with 38 K along with crystal structural analysis. This material may be regarded as an extension but the spacing layers look metallic conducting unlike the previous materials. This finding was immediately followed by Lohnert *et al.*⁴²

1.4 Parent Material and Superconductivity

1.4.1 Doping Effect

Intrinsic parent materials do not exhibit superconductivity, but become superconductors with relatively high T_c only by doping. In

this section, the doping effect is described with a focus on the 1111 and 122-types.

1.4.1.1 The 1111-type

The parent materials for the 1111-type have tetragonal crystal structure at room temperature, but transform into orthorhombic structure at lower temperatures. Pauli para-magnetism is shown at room temperature, but changes into anti-ferromagnetism at a slightly lower temperatures than that of the structural transitions.^{43,44} The magnetic structure of CaFeAsF (antiferromagnetic metal phase) measured by neutron diffraction at low temperature is shown in Fig. 1.6.^{45,46} Stripe-type antiferromagnetic ordering (parallel along *a*-axis but anti-parallel along *b*-axis) of the magnetic moment in the FeAs plane and anti-parallel ordering between the adjacent FeAs planes are observed.

Electrons are doped into the bulk when an element with more valence electrons is substituted, while holes are doped by substituting an element with fewer valence electrons. In both 1111 and 122-types, it is possible to substitute Fe or As in the conducting layer and La, Ba, O or F in the blocking layer. The former and latter are called "direct doping" and "indirect doping," respectively. With electrons doping by substituting O with F in LnFeAsO, the tetragonal-orthorhombic transition temperature and Neel temperature decrease, and superconductivity is induced in succession. The critical temperature (T_c) increases, reaches a maximum, and then decreases as the dopant level increases. The superconductivity occurs in the tetragonal phase and not in the orthorhombic phase due presumably to antiferromagnetic ordering in the orthorhombic phase in the 1111-type as shown in Fig. $1.7a.^{47-52}$ In contrast to previous reports, Martinelli *et al.*⁵³ recently reported serious retention of the tetragonal-orthorhombic structural transition by doping of F into SmFeAsO $_{1-x}$ F_x and proposed a new phase diagram they observed the presence of the orthorhombic phase below 130 K in the composition region showing superconductivity ($x \sim 0.2$, $T_c >$ 50 K) using high-resolution synchrotron X-ray diffraction analysis. The orthorhombic distortion was too small to be detected by a conventional X-ray diffraction instrument. The 1111-type contains



Figure 1.6 Crystal and magnetic structure of CaFeAsF. Crystal structure is tetragonal at room temperature (lattice parameters $a_T = b_T \sim 0.4$ nm, $c_T \sim 0.9$ nm), but transforms into an orthorhombic (lattice parameters $a > b \sim \sqrt{2a_T}$, $c \sim c_T$) at 120 K. In the antiferromagnetic phase (<118 K), the electron spins of Fe order parallel to the *b*-axis and opposite to the *a*-axis direction, aligning the total moment in the *a*-axis direction. Because spins order with inversion between neighboring FaAs planes, the *c*-axis length of the magnetic sub-lattice is twice of that of the crystal lattice.



Figure 1.7 Temperature versus composition phase diagram for (a) 1111-type and (b) 122-type. (Ts: structural transition temperature, T_N : magnetic transition (Neel) temperature, AFM: antiferromagnetic phase, PMM: paramagnetic metal phase, SC: superconducting phase).

at least four components (more than five if dopants are included), and precisely controlling its composition is very difficult. Even if starting materials are mixed at the correct composition ratio, the prepared substance contains an impurity phase whose composition differs from the nominal one for many polycrystalline materials. For example, the impurity phases of SmOF, SmAs and/or Sm_2O_3 are formed, and their concentrations increase as the x increases in SmFeAsO_{1-x} F_x , which shows the highest T_c .^{16,50-52,54,55} This situation is similar to that of other 1111-type materials containing rare-earth elements. The impurity phase by reactions, LnOF, is very stable, and consequently, difficult to erase. Kohler et al.56 demonstrated the conspicuous difference in composition between nominal and resulting $SmFeAsO_{1-x}F_x$ from quantitative analysis using an electron probe micro-analysis (EPMA); they noted that the measured F-content in a specimen with the nominal composition of SmFeAsO_{0.75} $F_{0.25}$ is ~0.12. Karpinski *et al.*⁵⁷ reported that without exception, single crystals of $LnFeAsO_{1-x}F_x(Ln = La, Pr, Nd, Sm, Gd)$ contain considerable oxygen deficiencies.

The first FeSC reported was formed by electron doping as LaFeAsO_{1-x} F_x where F occupied the O site as $(F_0 + e')$.⁵⁸ Adding to the substitution of F ($T_c = 55$ K for SmFeAsO_{1-x}F_x), various procedures for the electron doping have been reported, including the formation of an oxygen vacancy ($V_0 + e'$: $T_c = 55$ K for SmFeAsO_{1-x}) using a high-pressure synthesis, 59,60 substitution of Th for Ln (Th_{Ln}+e': $T_c = 56$ K for Gd_{1-x}Th_xFeAsO),^{61,62} and substitution of Co, Ni or Ir for Fe (Co_{Fe} +e': T_c = 18 K for $PrFe_{1-x}Co_xAsO$, $T_c = 23$ K for $CaFe_{1-x}Co_xAsF$, $Ni_{Fe}+2e'$: $T_c = 11$ K for LaFe_{1-x}Ni_xAsO, Ir_{Fe} +e': $T_c = 18$ K for SmFe_{1-x}Ir_xAsO).^{26,63-65} The optimum doping level is 0.1–0.2/Fe atom for each doping mode, and indirect doping appears to be more effective than direct doping in achieving a high T_c . Figures 1.8(a) and (b) show the ρ -T plots of undoped LnFeAsO (parent) and oxygen vacancy-doped LnFeAsO (superconductor), respectively.⁵¹ The change in slope at 100-150 K shown in the parent material indicates structural and magnetic phase transitions. Doping suppressed these changes and superconductivity emerges. Figure 1.9 shows the variation of maximal T_c attained for Ln = Pr, Nd, Sm, Gd and Dy in Ln-1111. The low T_c of Eu-1111 is tentatively attributed to the change in the formal valence of Eu (+3 to +2). Recently, a new electron-doping method was proposed, substitution of H^- for an O^{2-} site.⁴⁹ An advantage of this method is higher solubility limit of H^- at the O^{2-} site than F⁻ in the 1111 compounds. Figure 1.10 shows the phase diagram obtained for Sm1111 system. Electron-doping was possible up to 45%, which is \sim 4 times larger than that for F-substitution. As a consequence, the dome of superconductivity including overdoped regime was clarified, and it turned out that T_c remains at a high temperature in the very high electron-doped state.

Emergence of superconductivity by hole-doping was reported using substitution of Ln with Sr (Nd_{1-x}Sr_xFeAsO, $T_c = 13.5$ K at x = 0.2), but its shielding volume fraction by superconductivity is small.^{67,68}

1.4.1.2 The 122-type

Compared to the 1111-type, doping methods to generate 122-type superconductors are more diverse. $Ba_{1-x}K_xFe_2As_2$ ($T_c = 38$ K at



Figure 1.8 Temperature dependence of resistivity for select typical 1111-type (a) parent materials and (b) oxygen-deficient superconductors.⁵¹



Figure 1.9 Optimal T_c 's reported for Ln-1111 superconductors prepared by doping with an oxygen vacancy or F.⁸⁷

x = 0.4), which utilizes the indirect hole doping, has the highest T_c .²¹ No report on indirect electron-doping has been reported such as replacement of Ae sites with La³⁺ except the following case. This is due probably to the instability of La-doped 122 phase as suggested by the DFT calculations.⁶⁹ Muraba *et al.* synthesized Sr_{1-x}La_xFe₂As₂ using a high-pressure technique and obtained $T_c = 22$ K at x = 0.4.⁷⁰ Very recently, Katase *et al.*⁷¹ clarified the comprehensive phase diagram in Ba_{1-x}RE_xFe₂As₂ by metastable cation doping in



Figure 1.10 Phase diagram of $SmFeAsO_{1-x}H_x$.⁴⁹ Data on $SmFeAsO_{1-x}F_x$ are also indicated.

epitaxial thin film growth. Direct electron doping is performed by substitution of Fe²⁺ sites with Co²⁺ with an excess 3d electron such as Ba(Fe_{1-x}Co_x)₂As₂($T_c = 23$ K at x = 0.2).⁷² Similar to that for 1111-type materials, the optimum carrier concentration is 0.1–0.2/Fe.

Another feature of the 122-type is the emergence of superconductivity by substituting isoelectronic elements such as Ru (for Fe)^{73,74} or P (for As)⁷⁵ as shown in Fig. 1.11. Such an isovalent substitution into the 1111-type does not lead to a superconducting state.^{76–78} However, the superconducting state is induced by replacing As with P in BaFe₂(As_{0.68}P_{0.32})₂, ($T_c = 30$ K) and by substituting Rh for Fe in Ba(Fe_{1-x}Ru_x)₂As₂, ($T_c = 22$ K at x = 0.44). Due to a decrease in lattice parameter upon the isovalent element replacement, the induction of superconductivity was initially explained as a chemical pressure effect. However, this explanation is not applicable to the case of Ba(Fe_{1-x}Ru_x)₂As₂, where



Figure 1.11 Phase diagram in BaFe₂(As_{1-x}P_x)₂. Inset show the exponent *n* in $\rho(T) = \rho_0 + \alpha T^{n.75}$

the lattice parameter increases upon replacement. Brouet et al.79 investigated $Ba(Fe_{0.65}Ru_{0.35})_2As_2$ by transport measurement and angle-resolved photoemission spectroscopy (ARPES), and deduced a two-fold increase in the Fermi surface pocket compared to BaFe₂As₂, which results in increased carrier concentration of both electrons and holes, and significantly enhancement of the Fermi velocity. Furthermore, they suggested that Ru substitution weakens the electron correlation through the covalent effect of Ru compared to Fe. These considerations are consistent with a smaller effective mass and larger Fermi surface revealed from the measurement of the de Haas-van Alphen effect.⁸⁰ Unlike cuprate superconductors whose parent materials are Mott-type insulators, the parent materials of FeSCs are antiferromagnetic metals with sufficient conduction carriers. Hence, it is plausible for a part of parent materials that the primary effect of doping to FeSCs affects the band structure instead of controlling the carrier density.



Figure 1.12 Correlation between local structure and T_c . (a) T_c vs. bond angle (α) around Fe, (b) T_c vs. Pn(Ch) height from the iron-plane.

The phase diagram (Fig. 1.7b) of 122-type materials clearly differs from that of the 1111-type. In the 1111-type, the regions showing anti-ferromagnetism and superconductivity are separated or barely overlap, whereas the 122-type materials have antiferromagnetic regions with a high T_c . Because the composition showing the highest T_c corresponds to that with a magnetic transition temperature of 0 K, this phenomenon is discussed in terms of the quantum critical point.⁸¹

1.4.2 Local Structure and T_c

Several models to explain the relationship between the structure and superconducting properties have been reported from the earlier stage of FeSC research. Lee *et al.*⁸² first reported a good correlation, which is called Lee's plot hereafter, between T_c and the angle (α) of As–Fe–As in the FeAs layer. Figure 1.12a summarizes the data on various iron-based superconductors on the Lee's plot. The highest T_c in the oxide 1111-type series (LnFePnO) is observed in materials with α corresponding to a regular tetrahedron (109.47°) such as Gd-, Smand Nd-1111. In this figure, the highest T_c 's reported and the α values mainly for the parent materials at room temperature are plotted.

Intuitively, we can imagine an increase in the density of state on the Fermi surface by the degeneracy of the orbitals resulting from the high symmetry around the Fe atom. This model has been successfully applied to fluoride 1111-type (*Ae*FeAsF), by comparing CaFFeAs ($\alpha = 108^{\circ}$, $T_c = 22$ K) and SrFeAsF ($\alpha = 112^{\circ}$, $T_c = 7$ K) where Co is doped into both parent materials to introduce superconductivity.²⁶ The regular tetrahedron rule can be also applied to the 122-type; one material (*Ae*Fe₂As₂) with an α value close to 109.47° shows a high T_c (e.g., Ba_{1-x}K_xFe₂As₂ shows the highest T_c at x = 0.3–0.45). According to the structural analysis of BaFe₂As₂ under high pressure by Kimber *et al.*,⁸³ the changes in the structure in terms of lattice parameters and As-Fe-As bond angle are similar to those by the chemical doping with K. They emphasized that a structural change due to the chemical pressure effect is more important to drive superconductivity than carrier doping.

Kuroki et al.⁸⁴ who were inspired by Lee's plot, proposed a theoretical model to explain the relationship between the structure and $T_{\rm c}$. They extracted an important parameter, $h_{\rm Pn}$, which indicates the height of the pnictogen atom measured from the Fe plane, then calculated the changes in the electronic structure and magnetic properties with changes in $h_{\rm Pn}$. Their calculations indicate the appearance of the electron pocket γ on the Fermi surface around (π, π) in the unfolded Brillouin zone is sensitive to h_{Pn} and this Fermi surface controls the strength of the nesting effect, T_c , and the symmetry of the superconducting gap. They concluded that $T_{\rm c}$ increases with increases in h_{Pn} . Figure 1.12b plots this relationship where T_c 's and h_{Pn} 's are employed in same manner as in Fig. 1.12a. In Fig. 1.12a, materials showing high T_c 's are roughly localized around $\alpha = 109.5^{\circ}$ for the 1111-, 122-and homologous-types, but the deviation from the regular tetrahedron rule is found in the 111-type where LiFeAs ($\alpha \approx 103^{\circ}$) shows a higher $T_{\rm c}$ (~18 K) than NaFeAs $(T_{\rm c} \sim 9 \text{ K}, \alpha \sim 108.5^{\circ})$ or LiFeP $(T_{\rm c} \sim 6 \text{ K}, \alpha \sim 108.5^{\circ})$. Although rules cannot be deduced from the h_{Pn} - T_c relationship in Fig. 1.11, a positive correlation for each material type is observed and the discrepancy for the 111-type is at least resolved. However, several discrepancies remain. h_{Pn} of KFe₂As₂ is highest in superconductors belonging to the 122-type, but its T_c is low (~4 K).⁸⁵ For the 11-type, $h_{\rm Pn}$ increases with the Te content, but the $T_{\rm c}$ shows a maximum at x = 0.5 in FeSe_{1-x}Te_x.⁸⁶

Here we would like to discuss models for each type. Figure 1.13 shows the relationship between h_{Pn} and T_c for the doped Ln-1111-



Figure 1.13 Correlation between h_{Pn} and T_c of 1111-type superconductors of LnFeAsO_{1-x}F_x (closed marks) and LnFeAsO_{1-y} (open marks).⁸⁷

type superconductor.⁸⁷ Closed and open marks indicate F doped and O vacancy doped samples, respectively, and dotted lines denote the h_{Pn} 's of the parent materials. Except for two points of Pr-1111 where h_{Pn} 's were measured at low temperature (5 K), a positive correlation is roughly shown, suggesting the $h_{Pn}-T_c$ rule is applicable to the superconductors. However, it is impossible to apply this rule to an individual doping operation where h_{Pn} changes monotonically as the amount of dopant increases and the highest $T_{\rm c}$ emerges at the optimal composition due to such doping. For example, $(Ba_{1-x}K_x)Fe_2As_2$ is a complete solid solution system⁸⁸ where h_{Pn} of BaFe₂As₂ (1.358 Å) increase monotonically with an increase in x toward that of KFe_2As_2 (1.429 Å) and the highest $T_{\rm c}$ emerges at x = 0.37, $h_{\rm Pn} = 1.383$ Å (Fig. 1.14). The regular tetrahedron rule is effective on this material series. The T_c 's of alkaliintercalated FeSe compounds also are located at a good position on the Lee's plot (See Fig. 1.12).

Regardless of the high correlation between each structural parameter and T_c (α - T_c , h_{Pn} - T_c), several distinct deviations still



Figure 1.14 Correlation between T_c and local structural parameters (α and h_{Pn}) in Ba_{1-x}K_xFe₂As₂. Data were taken from ref. 88.

remain. Consequently, a structural parameter that is applicable to FeSCs as a whole has yet to be found. On the other hand, the unique characteristics of each type of FeSC have been determined as FeSC research has progressed. Hence, it is unclear whether a universal parameter to describe the characteristics of FeSCs as a whole exists.

1.5 Unique Characteristics of FeSCs

1.5.1 Multi-Band Nature of Fe3d

Figure 1.15 shows the calculated and observed density of state in LaOFeAs.⁸⁹ The electronic state of the Fermi level (E_F) controlling the transport property is formed by a complex tangle of five Fe3d orbitals, due to the small contribution of As, which is unlike cuprate superconductors where only Cu d_{x2-y2} contributes to the E_F . With five bands comprising E_F , multi-pockets appear on the Fermi surface. The energy levels of d_{x2-y2} , d_{xy} , and d_{yz} are sensitive to both the changes in the symmetry of the FeAs₄ tetrahedron and the carrier density. These energy level differences influence the shape and volume of the pockets on the Fermi surface. Consequently,



Figure 1.15 Calculated and measured density of states in LaFeAsO and LaFePO.⁸⁹ The contribution of pnicogen to the Fermi level is small.

these differences affect the strength of Cooper pair formation due to spin fluctuations and subsequently mediate T_c .^{84,90,91} As described in Section 4.2, the model proposed by Kuroki *et al.*⁸⁴ classifies T_c by the height of pnictogen (h_{Pn}) from the Fe plane. This model is attributed to the fact that h_{Pn} reflects the relationships between the three bands of the 3d orbitals (d_{x2-y2} , d_{xy} and d_{yz}) and E_F . Recently, the orbital fluctuation mechanism was proposed^{92,93} based on an experimental finding of a large reduction of share elastic modulus near the structural/magnetic transition.⁹⁴

1.5.2 Parent Material: Antiferromagnetic Metal

Metal compound superconductors such as MgB₂ do not exhibit magnetism and their conduction electrons induce superconductivity without doping. The parent materials of cuprate superconductors are antiferromagnetic insulators with a Cu magnetic moment of $\approx 1\mu_B$, which corresponds to nine electrons localized on the 3d orbitals. The parent materials of the 1111-or 122-type FeSCs are antiferromagnetic metals, and their magnetic moment per Fe atom is 0.4–0.9 μ_B which is much smaller than that due to the six electrons localized on Fe²⁺ with a high spin state (4 μ_B). The repulsive energy between 3d electrons in FeSC is approximately half that in cuprate. These results demonstrate the strong itinerancy of electrons in FeSCs.

In the parent compounds, 245 phase is totally different from others;⁹⁵ it is an insulator with a distinct band gap and high spin magnetic moment and high Need temperature (\sim 500 K) such as $3\mu_{\rm R}$. Apparent coexistence of AM and superconductivity is attributed to the nano-scale phase separation.95 The antiferromagnetic spin fluctuation and the multi-band effect discussed in the above section are two factors to drive the system into the superconducting state. A plausible pairing is thought via interpocket scattering of electrons between the hole pockets (around the Γ point) and electron pockets (around the M point), and leads to a pairing situation where an isotropic gap with opposite signs on each pocket (so-called S^{\pm} symmetry). However, recent finding of robust impurity effect and modestly high T_c of the 245 phase (in which the hole pocket almost disappears).⁹⁶ The symmetry of the superconducting gap is an exciting topic in research on the theory of superconductivity.

1.5.3 Impurity Robust T_c

Generally, T_c 's of superconductors decrease drastically upon doping with magnetic impurities such as Fe, Ni, and Co. However, compared to cuprate superconductors, an analogous amount of a magnetic impurity doped into FeSCs causes only a small decrease in T_c . Additionally, superconductivity often emerges in FeSCs upon magnetic ion doping. That is, the substitution of Fe²⁺ (3d⁶) by Co²⁺ (3d⁷) or Ni²⁺ (3d⁸) in the non-superconducting parent material induces superconductivity, similar to the result of electron doping into the FeAs layer. A similar result can be obtained by doping the 4d transition elements as shown in Fig. 1.16.⁹⁷

1.5.4 Large Critical Field and Small Anisotropy

The superconducting performance is estimated from the critical temperature (T_c), critical current (J_c), upper critical field (H_{c2}), and anisotropy. A large H_{c2} and small anisotropy are unique properties of FeSCs. It has been reported that $H_{c2}(0)$ is 80 T for the 122-type (200 T for the 1111-type), and the anisotropic ratio of the resistivity (γ) is four for the 122-type. $H_{c2}(0)$ is defined as the upper critical



Figure 1.16 Phase diagram of $Ba(Fe_{1-x}T_{Mx})_2As_2$.⁹⁷ T_M = Transition metal.

field at 0 K, and γ is defined as the ratio of the resistivity along the crystal axes directions, *a* and *c*, measured just above T_c . $H_{c2}(0)$ of FeSC is higher than that of MgB₂ (\approx 40 T), but is smaller than that of a typical cuprate (\sim 350 T for YBa₂Cu₃O_{7- δ}). The γ value for FeSC is compatible with that of MgB₂ (\approx 3.5), but is lower than that of a typical cuprate (30–270 for YBa₂Cu₃O_{7- δ}). These properties are favorable for practical applications such as electrical wires. Table 1.1 listed the properties of FeSCs, MgB₂ and cuprates. The values of γ , J_c and H_{c2} , for FeSCs are discussed in the next section.

1.5.5 Advantageous Grain Boundary Nature

High- T_c superconductors have zero power consumption and could be used to produce ideal electric power lines. The major obstacle in fabricating superconducting wires and tapes is grain boundaries the misalignment of crystalline orientations at grain boundaries, which is unavoidable for polycrystals, largely deteriorates critical current density for each superconductors. Recently advantageous

Materials	Fe pnictides	MgB ₂	Cuprates
Parent material	antiferromagnetic metal ($T_N \sim 150$ K)	non-magnetic metal	antiferromagnetic insulator ($T_N \sim 400$ K)
Fermi level	five Fe 3d orbitals	two B 2p orbitals	single Cu 3d orbital
T _c max.	56 K	40 K	$\sim 130 \text{K}$
Superconducting	Extended s-wave	Simple s-wave	d-wave
gap symmetry			
$H_{2}^{c}(0)$	100-200 T	$\sim 40 T$	\sim 350T (YBCO)
Magnetic impurity effect	robust	sensitive	sensitive
Anisotropy of conductivity	2-4 (122) 8-10 (1111)	~ 3.5	30-250 (YBCO)
			~ 1000(Bi2112)
Critical tilt angle for J_c	~°(Ba 122)		$\sim 5^{\circ}$ (YBCO)

Table 1.1 Comparison between three representative superconductors

grain boundary nature was reported for Co-doped Ba122 with a small anisotropy. Katase *et al.*⁹⁸ examined the transport properties through well-defined bicrystal grain boundary junctions with various misorientation angles (θ_{GB}) for cobalt-doped BaFe₂As₂ epitaxial films fabricated on bicrystal substrates and found that iron pnictide superconductors have advantages over cuprates with respect to these grain boundary issues. Figure 1.17 shows the J_c of Ba122:Co epitaxial thin films as a function of θ_{GB} . The J_c through bicrystal grain boundary, J_c (BGB) remained high (>1MAcm⁻²) and nearly constant up to a critical angle θ_c of ~9°, which is substantially larger than the θ_c of ~ 5° for YBa₂Cu₃O_{7- δ}. Even at $\theta_{GB} > \theta c$, the decay of J_c (BGB) was much slower than that of YBa₂Cu₃O_{7- δ}. Such grain boundary natures together with the high $H_{c2}(0)$ make the iron pnictides to be more promising materials for application to high J_c superconducting tapes.

1.6 Single Crystal

1.6.1 Growth of 1111-Type Crystals

After superconductivity of LaFeAsO was initially discovered, single crystal for Nd-1111-type and Sm-1111-type materials have been reported by Wen's group⁹⁹ and Kalpinski's group,¹⁰⁰ respectively.



Figure 1.17 Critical current density (J_c) of Co-doped BaFe₂As₂ epitaxial thin films as a function of bicrystal grain boundary (BGB) angle θ . (a) sample shape for J_c measurement, (b) J_c as a function of BGB. Data of YBCO are also drawn for comparison, (c) bicrystal grain boundary J_c normalized by In grain bridge J_c vs. θ , and (d) TEM photo around BGB. Dislocations with a periodic separation (I) is seen and the length continuously decreases with θ and I at the θ_{cri} is close to the coherent length.⁹⁸

For the 1111-type, the crystal growth was carried out using a flux of alkali halide under either atmospheric or high pressure. Although the high-pressure method can grow larger crystals within a short time,^{100–102} the instrument is large and expensive. Here, we introduce in the atmospheric pressure method reported by Jia *et al.*^{99,103} Powders of NdAs, NdF₃, Fe₂O₃, and Fe are mixed in a stoichiometric composition with the formula of NdFeAsO_{0.82}F_{0.18} and the mixture is pressed into a pellet, placed together with NaCl powder at a weight ratio of (NaCl:NdFeAsOF = 10:1), sealed in an evacuated quartz tube, and sintered at around 1050°C for 10 days. Afterwards, it is cooled at a rate of 3°C/h to 850°C, and

then the furnace is turned off for faster cooling. The resulting product contains mainly plate-like small crystals with lateral sizes ranging from 5 to 30 μ m and thicknesses of 1–5 μ m. Although larger plate-like crystals with a lateral size of 100 μ m have been obtained under high-pressure growth (3 GPa) for 1–2 days, the crystals are too small to operate by hand. Yan *et al.*¹⁰⁴ prepared doped LaFeAsO superconducting single crystals with a lateral size of several millimeters under atmospheric pressure in NaAs flux, but the dopant content has yet to be controlled. Because the scale of 1111-type single crystals is generally small, the focused ion beam (FIB) technique has been employed to shape specimens and contact electrodes with sub-micrometer dimensions.^{99–104}

1.6.2 Growth of the 122-Type Crystals

Single crystals of 122-type with a lateral size on the "millimeter" order can be prepared using a flux method with Sn or FeAs. Immediately after Johrendt's group²¹ reported superconductivity of (Ba,K)Fe₂As₂, several groups prepared single crystals of BaFe₂As₂ doped with K^{105,106} and Co¹⁰⁷ Plate shape single crystals measuring $1-2 \times 1-2 \times 0.05-0.1 \text{ mm}^3$ have prepared in the following manner.¹⁰⁵ Elemental Ba, K, Fe and As are added to Sn in the ratio of [(Ba,K)Fe₂As₂]:Sn = 1:48 as a starting material, and the mixture is placed in an MgO crucible. Then a second catch crucible containing quartz wool is set on top of this growth crucible. This assembly is sealed in a silica glass tube under approximately 1/3 atmosphere of argon gas. The sealed tube is heated to 850°C and cooled to 500°C over 36 h. Once the furnace reached at 500°C, the Sn flux was decanted from the (Ba,K)Fe₂As₂ crystals using a centrifuge.

Use of the FeAs flux is effective to obtain large crystals. According to Ni *et al.*¹⁰⁸ a Ba(Fe_{1-x}Co_x)₂As₂ single crystal with dimension of 12 × 8 × 0.8 mm³ can be prepared by mixing Ba, FeAs and CoAs with a ratio of 1:4(1 – *x*):4*x*. The mixture is placed into an alumina crucible, and then a second crucible is attached on the growth crucible and sealed in the same manner as the Sn case. This assembly is heated at 1180°C for 2 h and cooled over 36 h to 1000°C. Once the furnace reached at 1000°C the fluxis decanted from the Ba(Fe_{1-x}Co_x)₂As₂ crystals using a centrifuge.

Recently, the growth of a Ba_{0.6}K_{0.4}Fe₂As₂ crystal without a flux agent has been reported.¹⁰⁹ Excess K and As are mixed with starting materials of Ba, K, Fe, and As to compensate for evaporation loss. The mixture with a nominal composition of Ba_{0.6}K_{0.44}Fe₂As_{2.1} is placed in an alumina crucible and heated above 1200°C to melt completely in a tightly sealed stainless tube. It is subsequently cooled below 1050°C prior to turning off the furnace. Single crystals with a lateral size on the "millimeter" order are obtained using this method.

1.6.3 Characteristics of a Single Crystal

Similar to cuprate superconductors, FeSCs have a layered structure, but FeSCs are unique due to their small anisotropy. For instance, the resistivity of cuprate superconductors along the *a*- or *b*-axis direction at T_c (parallel to the CuO₂ conduction plane) is smaller than that along the *c*-axis direction with a ratio ($\gamma_{\rho} = \rho_c/\rho_{ab}$) of 30–250 for YBa₂Cu₃O_{7- δ}¹¹⁰ and over 1000 for Bi₂SrCaCu₂O₁₀.¹¹¹ This high anisotropy is a reflection of a thick blocking layer in cuprates. High anisotropies are also observed for the upper critical fields (H_{c2})¹¹² and the critical current density (J_c)¹¹³ in cuprate superconductors.

For FeSCs, early band-structure calculations suggest a twodimensional electronic structure.¹¹⁴ A high anisotropy in the resistivity with $\gamma_{\rho} \approx 100$ is reported for the non-superconducting parent compounds BaFe₂As₂¹¹⁵ and SrFe₂As₂¹¹⁶ as well as for superconducting Co-doped BaFe₂As₂.¹⁰³ In contrast, Tanatar *et al.*¹⁰⁴ reported that the ratio $\gamma_{\rho} = \rho_c/\rho_{ab}$ for Ba(Fe_{0.936}Co_{0.074})₂As₂ is about 3–5 at T_c , and this value is widely accepted. Moll *et al.*¹¹⁹ reported a higher γ_{ρ} (10 at T_c) for the 1111-type SmFeAsO_{0.7}F_{0.25} single crystal shaped by the FIB technique with thicker blocking layer than that of the 122type.

For polycrystalline materials, two different critical current densities, J_c^{local} and J_c^{global} , should be examined. The former is J_c of the intra-grain and the latter is the total J_c of the specimen, which includes contributions from the inter-grain and surface. Because the inter-grain suppresses J_c in many cases, J_c^{global} of polycrystalline specimen is considerably smaller than that of J_c^{local} . Factors responsible for the suppression at the inter-grain region are voids, cracks, impurity phases, and weak-links of grains, which are

remarkable in materials with high anisotropy. Such obstacles can be neglected $(J_c^{\text{global}} = J_c^{\text{local}})$ in single crystals. The anisotropy of J_c is observed in materials with structural anisotropy such as FeSCs. To evaluate them precisely, measurements using a single crystal are essential. Generally I_c attains a high current value on the order of $> 10^5$ A/cm² at 4 K for FeSCs, and direct measurement by the I-V relation is limited to the immediate vicinity of T_c . Thus, I_c is usually estimated from magnetization measurements (M-H curves) by applying Bean's model.¹²⁰ Figure 1.18 shows the I_c 's estimated by Tanatar *et al.*¹¹⁸ for Ba(Fe_{0.936}Co_{0.074})₂As₂($T_c = 23$ K) and by Moll *et al.*¹¹⁹ for SmFeAsO_{0.7} $F_{0.25}(T_c = 48 \text{ K})$, where J_c is the critical current density along the *ab*-plane direction measured by applying a magnetic field to the *c*-axis direction (H//c) and the *ab*-plane direction (H//ab), respectively. The I_c 's are 2.8×10^5 A/cm² and 2.2×10^6 A/cm² at 5 K for the 122 and 1111- types, respectively. In a broad range of temperature from $T_{\rm c}$ to 5 K, the magnetically determined in-plane and inter-plane critical current densities differ by a factor of three in the 122-type. Such a difference for the 1111type is small at low temperatures, but increases as the temperature increases.

Beside single crystals, the reported critical current densities include 1×10^4 A/cm² at 4 K of polycrystalline Ba_{0.6}K_{0.4}Fe₂As₂ prepared by the PIT method ¹²¹ and 4×10^6 A/cm² at 4 K of BaFe₂As₂:Co epitaxial film grown by pulsed laser deposition.¹²²

Figure 1.19 shows H_{c2} 's estimated by Ni *et al.*¹⁰⁸ for $(Ba_{0.55}K_{0.45})Fe_2As_2$ ($T_c = 32$ K) and by Moll *et al.*¹¹⁹ for SmFeAsO_{0.7}F_{0.25} ($T_c = 48$ K) where H_{c2} is the upper critical field measured by applying a magnetic field to the *c*-axis direction (H//*c*) and the *ab*-plane direction (H//*ab*) respectively. The measurement for a $(Ba_{0.55}K_{0.45})Fe_2As_2(T_c = 32$ K) single crystal indicates $H_{c2}^{//c} = 55$ T and $H_{c2}^{//ab} = 66$ T at 15 K, where the superscripts //*c* and //*ab* indicate magnetic fields applied parallel to the *c*-axis and the *ab*-plane, respectively. From the extrapolation of their H_{c2} -*T* plots, estimates for both $H_{c2}^{//ab}$ and $H_{c2}^{//c}$ readily exceed 80 T at 4 K. The anisotropy ($\gamma_H = H_{c2}^{//ab}/H_{c2}^{//c}$) is small, 1.2 at 15 K, and decreases with temperature in the temperature region of 32–14 K.¹²³ For a SmFeAsO_{0.7}F_{0.25} single crystal, $H_{c2}^{//ab}$ (which exceeds the measurement range up to 65 T at 36 K) is higher than that of the



Figure 1.18 J'_c 's (along the *ab*-plane direction) of Ba(Fe_{0.926}Co_{0.074})₂As₂ and SmFeAsO_{0.7}F_{0.25} single crystals for an applied field parallel to the *c*-axis and perpendicular to the *c*-axis (parallel to the *ab*-plane) calculated using Bean's model. ^{118,119}

 $H_{c2}^{//c}$ (60T at 15 K) in the entire temperature range. Additionally, the anisotropy of H_{c2} (γ_H) decreases monotonically from 6 at 48 K to 3.5 at 37 K as temperature decreases. From the extrapolation of this result, the estimated $H_{c2}^{//}$ exceeds 150 T and $H_{c2}^{//i}$ s greater than 100 T at 4 K. The 1111-type shows a higher H_{c2} and higher γ_H than those for the 122-type. The higher γ_H and γ_ρ of the 1111-type originate from the higher two-dimensionality, which is attributed to a thicker blocking layer than that in the 122-type.

1.7 Thin Film

1.7.1 1111-Type Compounds

Hiramatsu *et al.*¹²⁴ first succeeded in fabricating *in situ* epitaxial films of 1111-type compounds, LaFeAsO (La1111) films, on MgO



Figure 1.19 Anisotropic $H_{c2}(T)$ of $(Ba_{0.55}K_{0.45})Fe_2As_2$ and SmFeAs $O_{0.7}F_{0.25}$ single crystals for an applied field parallel to the *c*-axis and perpendicular to the *c*-axis (parallel to the *ab*-plane).^{108,119}

and LSAT substrates by PLD using a second-harmonic Nd:YAG laser (533 nm). The XRD patterns shown in Fig. 1.20 clearly indicated perfect *c*-axis and in-plane alignment of the as-grown film deposited using a F-doped LaFeAsO target with a nominal content of 10 at.%. The film showed a temperature dependence of the resistivity curve resembling that of undoped La1111, suggesting that F was not effectively incorporated in the film deposited at a substrate temperature of around 780°C. Since the 1111-type compounds also become superconducting by electron doping via the introduction of oxygen deficiency, they attempted post-annealing in a H₂ atmosphere. However, the H₂ annealing resulted in only a slight change in the lattice parameters and no superconductivity was induced. In contrast, Backen et al.¹²⁵ obtained superconducting LaFeAs(0,F) (F-La1111) thin films by an *ex situ* PLD method.¹²⁵ The precursor films deposited on LaAlO₃ substrates at room temperature from a LaFeAsO_{1-x} F_x (x = 0.25) target were annealed in a silica glass tube at approximately 1030°C. The annealed films



Figure 1.20 Epitaxial thin films of LaFeAsO grown on LSAT substrate by PLD.¹²⁴ XRD patterns and TEM photo of the resulting films are shown along the epitaxial relationship.

exhibited *c*-axis and in-plane orientations and a resistive T_c onset of 11 K, although zero resistance was not obtained. By optimizing the conditions of post-annealing with the bulk material having the target composition in a silica glass tube, they raised the T_c onset and T_c zero up to 28 and approximately 20 K, respectively.¹²⁶ However, the films showed weak-link behavior and a rather low self-field J_c on the order of 103 A/cm² at low temperatures.

1111-type compound thin films with higher T_c values have been realized by means of an MBE method. Kawaguchi *et al.*¹²⁷ first reported the successful *in situ* epitaxial growth of Nd1111 thin films on GaAs substrates, which are lattice-matched with Nd1111, though the window of the optimum growth conditions, especially for O_2 and As flux. They found to be narrow. In spite of the use of an F-containing source, NdF₃, the obtained films exhibited semiconducting behavior of the resistivity, indicating that the F content in the films was too low. Subsequently, they found that a long growth time of over 5 h resulted in a clear superconducting transition with a T_c onset and a T_c zero of up to 48 and 42 K, respectively. They also noticed the existence of an NdOF layer near the surfaces of the superconducting films and considered that this layer might supply F into the films. Moreover, by artificially depositing a NdOF/Nd1111 bilayer structure to accelerate F incorporation, they obtained superconducting F-Nd1111 films on MgO and CaF₂ substrates in addition to GaAs substrates with the highest T_c zero of 50 K on CaF₂, which is comparable to that of bulk F-Nd1111.^{128,129}

1.7.2 122-Type Compounds

The 122-type compounds have small anisotropy and high T_c values close to that of MgB₂ for the K-doped compounds. Carrier doping by the substitution of K or Co is easier than F doping in the 1111-type compounds, particularly, for thin film growth, because F tends to evaporate from film surfaces. Thus, the largest number of works on thin films has been focused on the 122-type compounds among the iron-based superconductors.

The first superconducting epitaxial films of the 122-type compound Sr(Fe,Co)₂As₂ (Co-Sr122) were synthesized on (LaSr) (Al,Ta)O₃(LSAT) single-crystal substrates by Hiramatsu *et al.*¹³⁰ by pulsed laser deposition (PLD) using a second-harmonic Nd:YAG laser ($\lambda = 532$ nm). The film deposited at a higher substrate temperature of 700°C clearly exhibits in-plane orientation and the epitaxial relationship (001)[100] SrFe₂As₂|(001)[100] LSAT. The films exhibited a T_c onset and a T_c zero of approximately 20 and 15 K, respectively. Although the transport critical current density (I_c) for the films was rather low, 20 kA/ cm^2 at 4.2 K, the measurements in a high magnetic field of up to 50 T using a pulse magnet revealed that the films have a nearly isotropic upper critical field and γ is close to 1 at low temperatures.¹³¹ Co-Sr122 films were also found to have rather high sensitivity to humidity. They underwent rapid degradation in water vapor, and, interestingly, undoped Sr122 epitaxial films were found to exhibit superconductivity below 25 K after exposure to humid air for 2-6 hours, which can possibly be attributed to the doping of water-related species such as 0^{2-} or OH⁻ in the I9 site between the Fe-As tetrahedron and the Sr atom in Sr122.132

Compared with Sr122, BaFe₂As₂ (Ba122) bulk polycrystal was found to be more stable in air. Katase *et al.*¹³³ confirmed that Co-doped Ba122 (Co-Ba122) epitaxial films prepared by PLD showed



Figure 1.21 Temperature dependence of resistivity and J_c in Co-doped BaFe₂As₂ epitaxial thin films grown on LSAT substrates. HQ denotes the films deposited under the improved conditions.

no appreciable change in the resistive T_c even after exposure to water vapor (dew point of 20-25°C) for 48 h, and thus had much higher stability against water vapor than Sr122 films. Such high stability was considered to be due to the smallest free space of the I9 site in Ba122 among the Ae122 compounds. The Co-Ba122 epitaxial films were also found to have higher crystallinity with an atomically flat surface and exhibit a sharper resistive transition than the Co-Sr122 films. Moreover, by increasing the purity of the Co-Ba122 target and optimizing the PLD conditions, they succeeded in directly fabricating Co-Ba122 epitaxial films with a narrow resistive transition width of $\Delta T_c = 1.1-1.3$ K and a self-field I_c of 1-4 MA/cm² at 4 K, as shown in Fig. 1.21, on both LSAT and MgO substrates.¹³⁴ The high- I_c film on LSAT was found to show a J_c peak for a field parallel to the *c*-axis that was larger than the peak for a field perpendicular to the *c*-axis even at a high field of 12 T at a low temperature of 4 K. This finding suggested the existence of caxis correlated defects or pinning centers in the film,¹³⁵ although the origin of the pinning centers is not yet clear. Iida et al. also fabricated Co-Ba122 epitaxial thin films on SrTiO₃ (STO), LSAT, and LaAlO₃ (LAO) substrates by PLD using a KrF excimer laser ($\lambda = 248$ nm) and found a strong correlation between the c/a lattice constant ratio and $T_{\rm c}$ onset,¹³⁶ though a systematic correlation between a and the lattice mismatch was not observed.



Figure 1.22 (a) Dependence of J_c on magnetic field parallel to the *c*-axis for Co-Ba122 thin films prepared on bare LSAT and SrTiO₃ (STO) substrates, a 50-unit-cell (u.c.)-thick BaTiO₃ buffer layer, and a 100-u.c.-thick STO buffer layer on LSAT. (b) Magnetic field angular dependence of J_c at 14 K and 1, 4, and 8 T for a Co-Ba122 thin film on STO/LSAT.¹³⁷

High-quality Co-Ba122 epitaxial thin films were also fabricated by using a buffer layer technique. Lee *at al.*¹³⁷ reported that the epitaxial quality of Co-Ba122 thin films was significantly improved by employing an STO or $BaTiO_3$ (BTO) template layer with a thickness of 50-100 unit cells on LSAT or other substrates as compared with the films directly prepared on the substrates by PLD. More interestingly, the epitaxial films on the template exhibited a very high J_c in magnetic fields parallel to the *c*-axis of up to 14 T, as shown in Fig. 1.22, indicating strong *c*-axis flux pinning. Co-Ba122 films on an optimized template (100 unit cells of STO) were found to exhibit a I_c peak for a field along the *c*-axis exceeding J_c for H//ab up to a high field of 12 T at 12 K and a large maximum pinning force of above 5 GN/m³. Recently, Katase et al.¹³⁸ reported high critical current densities $I_c > 1$ MA/cm² were realized in cobalt-dopedBaFe2As2:Co films on flexible metal substrates with biaxially textured MgO base-layers fabricated by an ion-beam assisted deposition technique. The films showed small inplane crystalline misorientations of 3° regardless of twice larger misorientations (7.3°) of the MgO base-layers, and exhibited high self-field I_c up to 3.5 MA/cm² at 2 K. These values are comparable to that on MgO single crystals and the highest I_{c} among iron pnictide superconducting tapes and wires ever reported. High in-field J_c suggests the existence of *c*-axis correlated vortex pinning centers.

K-doped Ae122 (Ae = Sr, Ba) has the highest T_c of 38 K among the 122-type compounds. The fabrication of such thin films is difficult because of the volatile and reactive nature of K. Lee et al.¹³⁹ first reported the synthesis of K-doped BaFe₂As₂ (K-Ba122) thin films by an ex situ PLD method in which an undoped Ba122 film deposited at room temperature was post-annealed with K shots in a silica glass tube. The films prepared on Al_2O_3 (0001) and LaAlO₃ (001) substrates exhibited a preferential *c*-axis orientation, and the former film showed a T_c onset and T_c zero of as high as 40 and 37.5 K, respectively. The in situ growth of epitaxial K-doped Ae122 films by a molecular beam epitaxy (MBE) method has recently been reported by Takeda et al.¹⁴⁰ They employed a chemically stable In-K alloy (In_8K_5) as a K source and found that the key to incorporating K into films is low-temperature growth (300-350°C) in a reduced As flux. The obtained K-Ba122 film exhibited a T_c onset and T_c end of 38.3 and 35.5 K, respectively, and substantially lower resistivity than that of the ex situ films. 8. However, because the K-doped films degraded immediately in an ambient atmosphere. Passivation is needed for further handling.

1.7.3 11-Type Compounds

The 11-type compounds have the lowest T_c among the iron-based superconductors. However, their simplest crystal structure and the pressure-induced significant increase in $T_{\rm c}$ straightforwardly lead to motivation for fabricating epitaxial films on lattice-mismatched substrates, which may show strain-induced T_c enhancement. Fabrication of the first 11-type compound thin film, an $Fe(Se_{0.5}Te_{0.5})$ film with a T_c zero of approximately 12 K, by a PLD method using a KrF excimer laser was reported by Wu *et al.*¹⁴¹ Subsequently, Wang *et al.*¹⁴² of the same group reported the properties of $FeSe_{1-x}$ thin films deposited on MgO substrates by a PLD method. They found that thin *c*-axis-oriented films did not undergo a structural transformation to a low-temperature orthorhombic phase and superconductivity, while (101) -oriented films deposited at a higher substrate temperature underwent such a structural transformation and had a T_c of approximately 8 K as observed in bulk FeSe_{1-x}. Similarly $FeSe_{1-x}$ superconducting thin films with (101) preferential



Figure 1.23 Epitaxial thin films of Fe(Se,Te). (a) *a*-axis and (b) T_c values vs film thickness on LAO (\circ), STO (\Box), and Y:ZrO (\Box). (c) ρ -*T* curves for several films on LAO with different thickness (9, 18, 36, 72, 150, 200, 280, and 420 nm). The inset shows the detail of the superconducting transition for some films.¹⁴⁶

orientation and T_c values close to the bulk value were prepared on various substrates including sapphire (0001), STO, and LAO by a PLD method.¹⁴³ However, no sign of strain-induced T_c enhancement was observed in these studies. Imai *et al.*¹⁴⁴ investigated the properties of Fe(Se_{0.5}Te_{0.5}) thin films deposited on eight different substrates and found no systematic *a*-axis contraction associated with the lattice mismatch. The film T_c was found to be rather strongly correlated with the degree of in-plane orientation and the lattice parameter ratio c/a.

On the other hand, Si *et al.*¹⁴⁵ observed an enhancement of T_c onset to 17 K in some of their Fe(Se_{0.5}Te_{0.5}) films prepared on STO substrates by a PLD method and suggested that the significantly reduced lattice constant *c* was related to the T_c enhancement. Bellingeri *et al.*¹⁴⁶ reported a more significant T_c enhancement up to 21 K in high-quality epitaxial Fe(Se_{0.5}Te_{0.5}) films on LAO and yttrium-stabilized zirconia (ZrO₂:Y) substrates with lattice constants slightly smaller than the *a*-axis constant for the bulk Fe(Se_{0.5}Te_{0.5}). The films exhibited a significant decrease in the *a*-axis lattice constant with increasing thickness, as shown in Fig. 1.23,