Crystal structure and phase diagrams of iron-based superconductors

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Since the discovery of high-temperature superconductivity (HTS) in iron-based compounds, a variety of systems with different spacer layers have been fabricated. Concurrently, considerable experimental and theoretical effort has been expended exploring the characteristics and source of HTS in iron-based superconductors. However, the origin of this HTS remains unresolved to date, while considerable debate exists regarding the underlying physics of the normal-state properties of iron-based compounds in particular. In this short review, we will briefly summarize the crystal structures and phase diagrams of the iron-based superconducting systems, aiming to discover potential avenues for the development of new superconductors with higher superconducting transition temperatures (T_c), along with indications of the specifics of the HTS mechanism in these substances.

In January 2008, Kamihara *et al.* [1] reported F-doped LaOFeAs iron-oxypnictide, a new superconductor with a superconducting transition temperature of $T_c \sim 26$ K. Soon after, Chen *et al.* [2] reported a new superconductor, SmFeAsO_{1-x}F_x, and elevated its T_c to 43 K under ambient pressure. It manifests the strong possibility that even higher T_c values may be obtained in such layered oxypnictides. The observed T_c of 43 K in SmFeAsO_{1-x}F_x exceeds the theoretical upper limit (39 K) predicted by the Bardeen-Cooper-Schrieffer (BCS) theory, providing a strong argument for considering layered iron-based superconductors as unconventional superconductors. In this article, we will review the crystal structures, synthetic techniques, and phase diagrams of iron-based superconductors.

CRYSTAL STRUCTURE

As early as 2006, Kamihara *et al.* [3] reported superconductivity in LaOFeP, which has the same crystallographic structure as LaFeAsO, but the value of T_c was only 4 K at that point. However, T_c can be significantly increased by F-doping, as had already been shown for the LaFePO_{0.94}F_{0.06} system, which has a T_c of 7 K [3]. At that time, the T_c of these compounds was too low to attract considerable scien-

tific interest, until the discovery of LaFeAsO_{1-x}F_x and SmFeAsO_{1-x}F_x [1,2,4,5]. Subsequently, a large amount of new iron-based superconductors were discovered, which can be classified into several families according to their structural characteristics, as shown in Fig. 1. The iron-based superconductors share a common anti-PbO-type Fe₂X₂ (X = P, As, Se, Te, etc.) layer within their structures. This Fe₂X₂ layer consists of edge-shared FeX₄ tetrahedra, and the discovered iron-based superconductors can be regarded as being comprised of an alternative stacking of the Fe₂X₂ layer along with spacer slabs. Considering the different structural characteristics of the spacer slabs, the iron-based superconductor can be classified using the following analogues:

(I) The 11 system stacking with only anti-PbO FeCh₂ layers, where Ch = Se, Te, S, and their combinations. Bulk FeSe can behave as a superconductor below approximately 10 K under ambient pressure [6], and the value of T_c is increased to 37 K through the application of external pressure [7,8]. By mixing Se and Te, T_c is increased to 15 K [9,10];

(II) The 111 system, which possesses an anti-PbFCl-type structure. Examples include LiFeP, LiFeAs, and NaFeAs [11–13]. LiFeAs and NaFeAs are superconducting when free of doping [12,13]. In the case of NaFeAs, however, only filamentary superconductivity exists, and bulk superconductivity requires doping with Co or Cu [14–16];

(III) The 122 system, which has a ThCr₂Si₂-type structure. Examples include AFe₂As₂ (A = Ba, Sr, Ca, Eu, K, Rb, and Cs) [17–20] and AFe₂Se₂ (A = Na, K, Rb, Cs, Tl, etc.) [21–24]. Superconducting 122 arsenides with other structure types also exist, such as SrPt₂As₂, which has a CaBe₂Ge₂-type structure [25], and BaPd₂As₂, with a CeMg₂Si₂-type structure [26]. The highest T_c of 122 arsenides is 38 K, which is realized in K- or Rb-doped BaFe₂As₂ or SrFe₂As₂ [17,20]. The intercalated FeSe superconductors also crystallize in a ThCr₂Si₂-type structure, including A_xFe_{2-y}Se₂ (with Fe vacancy in the FeSe layers) [21–24] and their derivative Fe-vacancy-free compounds, A_x(NH₃)_zFe₂Se₂ or A_x(NH₂)_y(NH₃)_zFe₂Se₂ (A = Li, Na, K, Ba, etc.) [27–29];

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Figure 1 Schematic view of the crystal structures of several typical iron-based superconductor families, in which A, Ae, Ln, and M represent alkali, alkali earth, lanthanide, and transition metal atoms, respectively.

(IV) The 1111 system with ZrCuSiAs-type structure. Examples include LnOFeAs (Ln = rare earth metal) [1,2,4,5], AeFFeAs (Ae = Ca, Sr, Ba, and Eu) [30,31], and CaHFeAs [32]. The highest bulk T_c (55 K) was achieved for the F-doped SmOFeAs or Sm-doped SrFFeAs systems [4,5,33];

(V) Systems with perovskite-like blocks intercalated between FeAs layers, such as $\text{Ae}_{n+1}\text{M}_n\text{O}_y\text{Fe}_2\text{As}_2$ (n perovskite layers sandwiched between the adjacent FeAs layers and $y \sim 3n-1$) [34–36], and $\text{Ae}_{n+2}\text{M}_n\text{O}_y\text{Fe}_2\text{As}_2$ [37,38] (n perovskite layers plus one rock-salt layer in each blocking layer between the adjacent FeAs layers, $y \sim 3n$). A T_c of greater than 40 K has been observed in these compounds [36];

(VI) Systems with skutterudite intermediary layers, which have been identified as $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$ (10-3-8) (referred to as α -phase) and $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_2\text{As}_2)_5$ (10-4-8) (referred to as β -phase) [39,40];

(VII) The FeSe-derived superconductor with completely new $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OH}$ spacer layer blocks between the adjacent FeSe layers, $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$ [41–43]. This superconductor exhibits a T_c of as high as 43 K. In this structure, the FeSe layer is the conducting block, while the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OH}$ layer is the charge reservoir block [42]. With alternate stacking of the $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OH}$ and anti-PbO-type FeSe layers, there exists a weak hydrogen bonding interaction between the layers (with quite a large H–Se distance of 3.078 Å) [42];

(VIII) Other composite structures, such as the $\text{BaTi}_2\text{As}_2\text{O}$ and BaFe_2As_2 composited $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$ superconductor [44].

Detailed crystallographic information for these classes of compounds can be found in previous reviews (for instance, Ref. [45,46]). Besides the classification according to the chemical formulae discussed above, the majority of the

iron-based superconductors can be divided into two larger classes based on the Bravais lattice, i.e., groups of tetragonal (11, 111, 1111, etc.) and body-centered tetragonal (122) structures. Among these substances, the electronic properties of body-centered tetragonal (122) materials tend to be more three-dimensional. Note that the compounds with perovskite-like blocks can have either tetragonal or body-centered tetragonal structures, depending on the presence of a rock-salt layer.

As a result of the large amount of available data concerning crystal structure and the corresponding T_c for iron-based superconductors, a specific relationship between the structure parameters and T_c was found [47,48]. The bond angle (α) of As–Fe–As, which reflects the distortion of the FeAs_4 tetrahedron, was thought to be closely related to the superconductivity of this material [47]. As shown in Fig. 2a, the maximum T_c in a FeAs-based superconducting system was achieved when the FeAs_4 tetrahedron was perfectly regular, with $\alpha = 109.47^\circ$. However, Fe(Se,Te) does not follow this rule, and the maximum T_c is obtained for $\alpha \sim 100.8^\circ$. Also, among the intercalated FeSe superconductors, $\text{Li}_{0.6}(\text{NH}_2)_{0.2}(\text{NH}_3)_{0.8}\text{Fe}_2\text{Se}_2$ and $(\text{Li}_{0.8}\text{Fe}_{0.2})\text{OHFeSe}$, which exhibit values of T_c higher than 40 K, have values of $\alpha = 102.93(6)^\circ(\times 2)$ and $103.2(2)^\circ(\times 2)$, respectively [28,42], which are less than those observed for $\beta\text{-Fe}_{1+\delta}\text{Se}$ ($103.9^\circ \times 2$) [49]. These facts suggest that distortion of the tetrahedron in FeSe-derived superconductors could enhance the superconductivity [42], in contrast to the concept that the ideal FeAs_4 tetrahedron is preferable for superconductivity in FeAs-based superconductors. Another typical relationship is the dependence of T_c on the height of the anion (As, P, Se, and Te) from the Fe layer (h), as shown in Fig. 2b [48]. The value of h depends on the anion type, and increases in or-

Figure 2 (a) Relationship between the As(top)-Fe-As(top) bond angle, α , and the T_c of iron-based superconductors. Reprinted with permission from Ref. [47] (Copyright 2012, Elsevier). (b) General anion height dependence of T_c for iron-based superconductors. Reprinted with permission from Ref. [48] (Copyright 2010, IOP Publishing). (c) Anion height-dependence of T_c for FeSe-derived superconductors [41,42].

der from FeP, FeAs, FeSe, to FeTe. For the FeAs-based 1111 phase, as the substitutions of Nd and Sm for La increase h to approximately 1.38 Å, T_c increases abruptly from 26 to 55 K, which is the maximum bulk value among all the Fe-based superconductors. FeP-based superconductors have relatively small h (compared with the optimal 1.38 Å) and, as a result, their T_c values are significantly lower than those in FeAs-based superconductors. For example, in the La-1111 phase, as P is replaced by As, T_c is dramatically enhanced from 7 to 26 K and accompanied by increasing h . After crossing this maximum, the T_c of TbFeAsO_{0.7}, Ba_{0.6}K_{0.4}Fe₂As₂, NaFeAs, and LiFeAs decrease in order of further increases in h . The data obtained for optimally doped FeSe_{1-x}Te_x and FeSe_{0.57}Te_{0.43} seem to follow the same trend. As a result, this h -dependence of T_c seems to be universal for 1111, 122, 111, and 11 iron-based superconductors. Although the maximum T_c of superconductors with a thick blocking layer remains unconfirmed, the data obtained for the 42622 superconductor obey the same universal curve, apart from a small deviation, which may suggest that the enhancement of the two-dimensional characteristic could induce a T_c greater than 56 K. Although such a universal relationship exists between h and T_c , an exception does, in fact, exist in the case of FeSe-derived superconductors. As shown in Fig. 2c, for FeSe-derived materials, a minimum T_c value (instead of a maximum) can be observed at $h \approx 1.45$ Å [41,42], as shown in Fig. 2b. This may suggest the existence of some new, currently unknown, underlying physics in FeSe-derived superconductors compared with that of FeAs-based materials.

PHASE DIAGRAMS

Chemical doping or external/chemical pressure has been applied to the parent compounds of iron-based superconductors in order to obtain superconductivity. Investigation of the relevant phase diagram is very helpful for understanding

the mechanism of this superconductivity. Hence, one can clearly see how the superconductivity emerges in response to chemical doping or external pressure (see Fig. 3) [50–58]. In general, the parent compound of an iron-based superconductor is an antiferromagnetic (AFM) bad metal, as shown in Fig. 4 [59,60]. Taking into account the fact that the parent compounds are usually poor metals, the mechanism of this AFM was historically ascribed to the spin-density-wave (SDW) ordering of itinerant electrons [59,61]. In contrast, the AFM in cuprate parent compounds arises from the superexchange of local moments [62]. The applicability of the itinerant electron model to pnictides was strongly supported by earlier angle-resolved photoemission spectroscopy (ARPES) experiments [63] and the first-principle calculations [64–67], which indicated that the Fermi surfaces of the parent compounds have perfect Fermi nesting conditions. However, in subsequent experiments, the simple itinerant electron model was found to provide an incomplete description, and a model with coexisting itinerant electrons and local moments should therefore be considered in order to obtain a comprehensive understanding of AFM in iron-based superconductors [68].

The parent compounds of iron-based superconductors have magnetic structures, as shown in Figs 4a and 4b. Neutron diffraction experiments have revealed that the magnetic wave vector in LaOFeAs is $(1/2, 1/2, 1/2)_T = (1, 0, 1/2)_O$, where T and O indicate tetragonal and orthorhombic phases, respectively, and the magnetic moment per Fe is $0.36\mu_B$. In LaOFeAs, the in-plane magnetic spins of the Fe atoms are arranged as shown in Fig. 4a. The spins lie within the ab plane, and are aligned antiferromagnetically along the orthorhombic a axis and ferromagnetically along the orthorhombic b axis [60,61,69]. The in-plane magnetic alignment for all the parent compounds of FeAs-based superconductors (111, 122, and 1111 systems) is similar to that of LaOFeAs. While the interplane spin alignment de-

Figure 3 Typical electronic and magnetic phase diagrams of several series of iron-based superconducting systems [50–58]. Reprinted with permission from (a) Ref. [50] (Copyright 2012, Nature Publishing Group), (b) Ref. [51] (Copyright 2009, Nature Publishing Group), (c) Ref. [52] (Copyright 2008, Nature Publishing Group), (d) Ref. [53] (Copyright 2009, IOP Publishing), (e) Ref. [54] (Copyright 2010, American Physical Society), (f) Ref. [55] (Copyright 2012, Nature Publishing Group), (g) Ref. [56], (h) Ref. [57], and (i) Ref. [58] (Copyright 2010, the Physical Society of Japan).

depends on the system, the spins in LaOFeAs, NdOFeAs, and BaFe₂As₂, for instance, are antiferromagnetically aligned along the *c* axis, while those in CeOFeAs and PrOFeAs are ferromagnetically aligned along the *c* axis [60]. Fe_{1+x}Te exhibits a very different alignment formation from that seen in FeAs-based compounds, and has quite complicated magnetic structures. In the AFM state, Fe_{1+x}Te has a magnetic wave vector (1/2, 0, 1/2) (see Fig. 4b) [70,71], that is, the spins align in a dual-AFM stripe in the crystallographic direction with a magnetic moment of 2.03μ_B per Fe atom (for *x* = 0.076) [71]. It is worth noting that the easy axis of the magnetic order in A_xFe_{2-y}Se₂ superconductors is the *c*-axis [72], which is distinct from the in-plane magnetic-ordered alignment of spins in FeAs-based compounds. At

present, it is widely believed that the AFM order with very high transition temperature (~500 K) and large moment (~3.3 μ_B/Fe) in A_xFe_{2-y}Se₂ is phase-separated from the superconductivity.

Through various types of chemical doping or the application of external pressure, the AFM order is suppressed and the ground states can be effectively tuned from AFM to superconducting phases. They then exhibit a quite universal phase diagram (see Fig. 3), which is similar to that of cuprate superconductors. This may suggest a possible common mechanism in both high-*T_c* superconductor families. In fact, with cooling from room temperature, the parent compounds first exhibit an interesting structural transition from a high-temperature tetragonal structure to a low-tem-

Figure 4 (a) In-plane spin alignment in the 111, 122, and 1111 FeAs-based systems [60,69]. (b) In-plane spin alignment in the 11 system [70,71].

perature orthorhombic structure, followed by the AFM transition [59]. The structural transition temperature (T_s) is usually slightly higher than or equal to the AFM transition temperature (T_N) (see Fig. 3). Obvious anomalies associated with the structural and magnetic transitions can be observed in the transport measurements, as shown in Fig. 5 [73,74]. Such structural transition is ascribed to electron-driven phase transition rather than pure structural effects, and strongly couples to the subsequent AFM transition [75–78]. The underlying mechanism of the structural

transition is also beyond the capacity of the simple itinerant electron model.

By tuning doping with different chemicals to a moderate level, superconductivity can be achieved for either hole- or electron-type carrier cases. As shown in Fig. 3, both structural and AFM transitions are suppressed continuously by doping with either hole- and electron-type carriers. Meanwhile, superconductivity emerges above the critical doping level and may coexist with the suppressed AFM order in part of the phase diagram. At first, T_c is enhanced with increased doping levels. It then reaches a maximum at the so-called “optimal doping level” and finally decreases to zero with further increased doping. The highest T_c in bulk materials, up to 55 K, was obtained for F-doped SmOFeAs [4,5,33], while values of T_c of up to ~100 K have been reported in single-layer FeSe film [79–83]. Typically, the superconducting region below the optimal doping level in the phase diagram is defined as the “underdoped superconducting region”. This is the same term as that used for cuprates. The area above the optimal doping level, where T_c is suppressed, is called the “overdoped superconducting region”. The entire superconducting region has a dome-like shape in the phase diagram.

One of the most important issues in iron-based superconductivity is the coexistence of the superconductivity with the AFM/SDW order. In F-doped LaOFeAs [84], PrOFeAs [85], and NdOFeAs [86], as shown in Figs 3a and 3b, the structural and AFM/SDW transitions vanish

Figure 5 Temperature dependence of resistivity for the: (a) 1111 system (polycrystalline SmO_{1-x}F_xFeAs) [Reprinted with permission from Ref. [73] (Copyright 2008, American Physical Society)]; (b) 122 system (hole-doped Ba_{1-x}K_xFe₂As₂ and electron-doped Ba(Fe_{1-x}Co_x)₂As₂ single crystals). Reprinted with permission from Ref. [74].

abruptly at a certain doping level, exhibiting a step-like behavior, and the superconductivity then emerges. There is no coexistence region for AFM/SDW ordering and superconductivity in the phase diagrams of these 1111 materials. In F-doped CeOFeAs [52], the structural and AFM/SDW transitions disappear continuously, but there is also no coexistence between the AFM/SDW ordering and superconductivity; the superconductivity simply appears when the AFM/SDW ordering is completely suppressed. These phases seem to be connected by a quantum critical point (QCP). In F-doped SmOFeAs [51], the structural and AFM/SDW transitions also go to zero continuously, but a region exhibiting coexistence between the AFM/SDW ordering and superconductivity exists. This suggests that the destruction of the long-range magnetic order is not an essential condition for the emergence of superconductivity. Such a coexistence of AFM/SDW ordering and superconductivity has been widely observed in 122 and 111 materials [14,15,53,54], but not in 1111 materials. The phase diagram of the 1111 system should therefore be re-examined in order to determine whether the coexistence of SDW and superconductivity occurs in LaOFeAs and CeOFeAs systems.

For the doped 122 materials, the question of whether the AFM/SDW and superconducting states coexist microscopically or are phase separated has received considerable attention. For hole doping with K, early studies on powder samples using techniques such as ^{75}As nuclear magnetic resonance (NMR) [87], μSR [88], and magnetic force microscopy (MFM) [88] consistently indicated the existence of both magnetically ordered and nonmagnetic regions, as expected for microscopic phase separation. Analyses of microstrains measured using X-ray, neutron diffraction and, later, ^{75}As NMR techniques on single crystals also supported the occurrence of electronic phase separation. In contrast, ^{57}Fe -Mössbauer measurements detected complete magnetic ordering in a K-doped BaFe_2As_2 sample, consistent with that expected based on the microscopic coexistence of the AFM/SDW and superconducting states [89]. Recently, Li *et al.* [90] presented unambiguous ^{75}As NMR evidence that AFM/SDW ordering and superconductivity coexist microscopically in the case of high-quality underdoped $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ single crystals. Considering the sample quality in the earlier studies, the microscopic coexistence of AFM/SDW ordering and superconductivity is most likely an intrinsic phenomenon in K-doped BaFe_2As_2 . In addition, for Co-doped 122 samples, both ^{75}As NMR [91] and μSR measurements [92] have also indicated the microscopic coexistence of superconductivity and AFM/SDW ordering. Further, in isovalently doped 122 materials (P-doped BaFe_2As_2 and Ru-doped BaFe_2As_2), the microscopic coexistence of superconductivity and AFM/

SDW ordering has been confirmed by NMR experiments [93]. As a result, it can be concluded that the microscopic coexistence of superconductivity and AFM/SDW ordering is universal in FeAs-122 systems. Furthermore, neutron diffraction measurements conducted on Co-doped samples ($x = 0.04$ and 0.047) [94,95] have indicated that the magnetic Bragg peak intensity of the AFM/SDW state is suppressed when entering the superconducting state, suggesting a very strong interaction between the superconductivity and SDW ordering. Such suppression can be attributed to the same electrons participating in both the SDW and superconductivity, so that the phase coexistence scenario is favored.

The evolution of finite-temperature electronic behavior with varying doping levels is also interesting and has been studied intensively. F-doped SmOFeAs can be taken as an example to illustrate the evolution of finite-temperature electronic behavior with F content, as shown in Fig. 5a [73]. Here, the low-temperature resistivity can be well fitted against $a + bT^n$, and the fitting parameter, n , shows a systematical change from 2.3 to 1 with increasing F content, from $x = 0$ to 0.15. It is intriguing that the temperature dependence of the low-temperature resistivity just above T_c changes to T -linear dependence with an increase in F content from $x = 0.14$ to 0.15, suggesting that a QCP appears in the region of $x = 0.14$. This occurs at the same time as the suppression of the AFM/SDW order. Such evolution of the finite-temperature electronic behavior has also been widely observed in other iron-based superconductors, such as the P-doped BaFe_2As_2 system [96,97]. Particularly, the scattering of charge carriers by fluctuation associated with the QCP, which is widely used to explain the T -linear resistivity in heavy-fermion metals [98], has been considered as a possible explanation for the T -linear resistivity observed in iron-based superconductors.

Besides the structural and magnetic transitions, an unexpected in-plane electronic anisotropy begins to emerge at temperatures well above T_s (as shown in Figs 3f and 3g). This is indicated by the resistivity, reflectivity, and ARPES measurements of detwinned single crystals of underdoped 122 materials [98]. As shown in Fig. 6a [99,100], this in-plane electronic anisotropy appears for a tetragonal structure at temperatures well above T_s , with a new temperature scale (T') (as marked in Figs 3f and 3g) [55,56]. This anisotropy has been attributed to the formation of electronic nematicity, a unidirectional self-organized state that breaks the rotational symmetry of the underlying lattice [99]. On the hole-doped side, the in-plane electronic anisotropy decreases very rapidly and has extremely small values. It can even exhibit sign reversal in anisotropy of in-plane resistivity (sign of $\rho_b - \rho_a$) at some relatively high doping levels [101–104]. In sharp contrast, the in-plane electronic anisotropy

Figure 6 (a) Anisotropic in-plane resistivity in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ single crystals. Reprinted with permission from Ref. [100] (Copyright 2010, American Association for the Advancement of Science). (b) Studies on the effect of impurity scattering on in-plane anisotropy in doped BaFe_2As_2 single crystals. Reprinted with permission from Ref. [102] (Copyright 2013, American Chemical Society).

was first enhanced on the electron-doped side and gradually disappeared with further doping [99,100]. The electronic nematicity revises our understanding of the phase diagram of normal states, but its origin has been quite controversial.

Recently, annealing experiments (see Fig. 6b) and scanning tunneling microscope (STM) results have revealed that the in-plane electronic anisotropy is most likely triggered by dopant atoms [102,105,106]. STM analysis of Co-doped

CaFe_2As_2 has revealed that substituting Co for Fe atoms generates a dense population of identical anisotropic impurity states. These impurity states then scatter quasiparticles in a highly anisotropic manner, suggesting that anisotropic scattering by dopant-induced impurity states is the source of the electronic nematicity [106]. However, determining whether this model is applicable to all 122 materials that exhibit electronic nematicity requires further investigation.

The iron chalcogenide, $\text{Fe}_{1+y}(\text{Te}_{1-x}\text{Se}_x)$, has the simplest structure of the iron-based superconductors [6,9,10]. Although its Fermi surface is similar to that of iron pnictides [107,108], the parent compound, Fe_{1+y}Te , exhibits an AFM order with an in-plane magnetic wave vector $(\pi, 0)$. This is in contrast to the parent compounds of iron pnictides, in which the magnetic order has an in-plane magnetic wave vector, (π, π) , that connects the hole and electron parts of the Fermi surface. Moreover, as mentioned above, the spin alignment configuration in the magnetically ordered state in Fe_{1+y}Te is distinct from that in iron-pnictide parent compounds. For $\text{Fe}_{1.141}\text{Te}$, a tetragonal-orthorhombic structural transition and an incommensurate magnetic wave vector, q , of $(\pm\delta, 0, 1/2)$ have been reported [71]. With decreasing excess Fe concentration, the incommensurate magnetic wave vector transitions continuously change to a commensurate magnetic wave in $\text{Fe}_{1.076}\text{Te}$. Furthermore, the superconductivity tends to be suppressed with greater excess Fe content [109,110]. The phase diagram of $\text{Fe}_{1+y}\text{Te}_{1-x}\text{Se}_x$ with a low excess Fe concentration, is shown in Fig. 3i [58]. As can be seen in this figure, the structural transition from the high-temperature tetragonal phase to the low-temperature monoclinic phase in Fe_{1+y}Te occurs at the same temperature as the AFM transition. At the other side of the $\text{Fe}_{1+y}(\text{Te}_{1-x}\text{Se}_x)$ phase diagram, FeSe_{1-x} exhibits superconductivity below 10 K. A structural transition also occurs in this material, from the high-temperature tetragonal to the low-temperature orthorhombic phase, but without any magnetic order following [111], which is in contrast to other iron-based superconductors. The tetragonal-orthorhombic structural transition observed in FeSe is suppressed with increasing Te concentration, and the highest T_c appears in the tetragonal phase near $x < 0.5$. With a further increase in Te content, the value of T_c reduces, the AFM ordering accompanying the tetragonal-monoclinic distortion appears, and the bulk superconductivity disappears. As shown in Fig. 3i, a miscible region (A + B) exists at approximately $x = 0.7$ to 0.95, at which phase separations occur.

As mentioned above, external pressure can also be used to tune the magnetism and superconductivity. It can be seen in Fig. 7a [112] that, in the majority of iron-pnictide systems, the application of pressure can enhance T_c efficiently, provided the pressure is below a moderate value. The value

of T_c can then be suppressed as the pressure increases further, for example, in doped LaFeAsO [113], underdoped 122 systems [114], and doped NaFeAs [16,115,116]. In particular, superconductivity can be induced by pressure in non-superconducting LaOFeAs and AeFe_2As_2 ($\text{Ae} = \text{Ca, Sr, Ba, Eu}$), which is accompanied by the suppression of the AFM/SDW transition in these systems [117,118]. In fact, suppression of the AFM/SDW transition by pressure can be observed for all the underdoped samples, as shown in Fig. 7b, provided a magnetic transition exists. Fig. 7b also demonstrates that pressure can expand the superconducting region to a lower doping level [119]. It should be noted that external or chemical pressure has an obvious effect on the magnetism in the FeAs or FeSe layer, but has a negligible influence on the magnetic order located outside these layers. For example, the external pressure does not change the AFM transition temperature of Eu^{2+} ions in EuFe_2As_2 and doped EuFe_2As_2 [118,120]. Moreover, the chemical pressure produced by S substituted in place of Se in $\text{Li}_{0.8}\text{Fe}_{0.2}\text{OHFeSe}$ has no effect on the AFM transition in the $\text{Li}_{0.8}\text{Fe}_{0.2}\text{OH}$ layer [121]. In FeSe , as shown in Fig. 7d, T_c can also be improved from 8 K at ambient pressure to 37 K at approximately 9 GPa, but then decreases with further increase in pressure [7]. In some compositions of $\text{K}_{1-x}\text{Fe}_y\text{Se}_2$ and $\text{Cs}_{1-x}\text{Fe}_y\text{Se}_2$ crystals, this hump-shaped pressure dependence of T_c can also be observed [122]. More generally, however, the suppression of T_c by pressure can be seen in $\text{K}_{1-x}\text{Fe}_y\text{Se}_2$ samples [122–124], where T_c goes to zero at approximately 10 GPa [123,124]. The most intriguing aspect of $\text{K}_{1-x}\text{Fe}_y\text{Se}_2$ is that a new superconducting state emerges with further increases in pressure, exhibiting a significantly higher T_c (~48 K at approximately 12 GPa), as shown in Fig. 7e [123]. It is apparent that the pressure dependence of T_c actually depends on the detailed materials. For example, in contrast to the behavior observed in doped LaOFeAs , monotonic suppression of T_c can be obtained in doped NdOFeAs and SmOFeAs systems, as shown in Fig. 7a [112].

The contrasting pressure-dependence behavior of T_c among different systems was previously thought to be related to the specific crystallographic detail of each substance. As discussed above, this can be reflected by an empirically inverse V-shaped dependence of T_c on anion height from the Fe layer in iron-pnictide compounds, with the optimal T_c occurring at $h_0 \gg 1.38 \text{ \AA}$ [48]. For example, doped LaOFeAs samples are located on the side of the diagram having values of h that are significantly smaller than h_0 , and external pressure causes these systems to shift to the area close to h_0 [125]. This results in a dramatic increase in T_c . However, for doped SmOFeAs and NdOFeAs with T_c of approximately 55 K, the anion heights from the Fe layer are almost equal to h_0 [48]; thus, any applied pressure will suppress T_c , because this pressure will separate the anion height

Figure 7 Phase diagrams under external pressure. (a) External-pressure dependence of T_c for several typical iron-pnictide compounds [112,115]. Reprinted with permission from Ref. [112] (Copyright 2011, American Physical Society) and [115] (Copyright 2009, IOP Publishing). (b) Doping-dependent phase diagram of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ under an applied pressure of 0 and 2.4 GPa. Reprinted with permission from Ref. [119] (Copyright 2009, American Physical Society). (c) Evolution of As-Fe-As α -value for $\text{NdO}_{0.85}\text{FeAs}$ ($T_c = 51$ K at ambient pressure) under external pressure (red circles). Reprinted with permission from Ref. [128] (Copyright 2009, the Physical Society of Japan). (d) External-pressure-dependent phase diagram of $\text{Fe}_{1.01}\text{Se}$. Reprinted with permission from Ref. [7] (Copyright 2009, Nature Publishing Group). (e) External-pressure dependence of T_c for $\text{K}_{0.8}\text{Fe}_{1.7}\text{Se}_2$, $\text{K}_{0.8}\text{Fe}_{1.78}\text{Se}_2$, and $\text{Tl}_{0.6}\text{Cs}_{0.4}\text{Fe}_{1.67}\text{Se}_2$. Reprinted with permission from Ref. [123] (Copyright 2012, Nature Publishing Group). (f) Anion height dependence of T_c under external pressure for FeSe samples (blue triangular circles). Reprinted with permission from Ref. [126] (Copyright 2010, American Physical Society).

of the system from h_0 . The pressure dependence of T_c in FeSe also seems to exhibit a very close relationship with the anion height from the Fe layer [126], as shown in Fig. 7f. However, from our study incorporating other FeSe-derived superconductors, as mentioned above, the anion height dependence of T_c in FeSe-derived systems may have a shape that is distinct from that obtained for iron-pnictide superconductors, as can be seen in Fig. 3c. The maximum value of T_c was thought to be clearly obtained in iron-pnictide compounds, when the FeX_4 tetrahedron achieved a regular shape [127]. However, the correlation between T_c and the Se-Fe-Se α -value discussed above has suggested that a regular FeSe_4 tetrahedron may not be a prerequisite for higher T_c [42]. In fact, the results of pressure studies on $\text{NdO}_{0.85}\text{FeAs}$ also imply that the regularity of the FeAs_4 tetrahedron may have less correlation to T_c than the anion height. Here, the As-Fe-As α -value changes very slightly (see Fig. 7c), in spite of the large decrease in T_c from 51 to 36 K in response to a change in pressure from ambient to 8 GPa [128].

Despite certain differences in the doping-dependent phase diagrams of the various iron-based superconductors,

a close inspection of Fig. 3 indicates that some common features exist. For example, all systems exhibit an AFM/SDW state for the parent compounds, which is suppressed with doping, while superconductivity is induced with further doping. A strong similarity to the generic phase diagram of cuprates is suggested, which provides evidence for the interplay between magnetism and superconductivity in Fe-based materials.

In summary, we have briefly reviewed the crystal structure features of all iron-based superconductors. It is notable that the superconductivity is not, in fact, directly related to the thickness of the spacer slabs between adjacent conducting FeAs/FeSe layers. This is in sharp contrast to the strong dependence of the superconductivity in cuprates on the distance between the CuO_2 planes. Instead, the superconductivity in iron-based superconductors has obvious dependence on the crystallographic parameters (such as the height of the anion from the Fe layer or the anion-Fe-anion angle). It should be noted that this indicates that the mechanism of superconductivity in iron-based superconductors is somewhat different from that in cuprates, although considerable effort has been expended in attempting to

unify the origins of the high-temperature superconductivity exhibited by these two superconducting families. However, despite certain subtle differences between the phase diagrams of the various iron-based superconductor systems, some common features that are extremely similar to cuprate characteristics have been observed, which causes researchers to believe that the interplay between magnetism and superconductivity plays a crucial role in both high-temperature superconducting families. On the other hand, the mechanism causing the coexistence of the AFM/SDW order and superconductivity, along with the nature of the notable electronic anisotropy (possibly nematicity) in the underdoped region, which may possibly be closely related to the occurrence of superconductivity in iron-based superconductors, remain unresolved at present. It appears that significantly more research is required, and it is hoped that this review will provide some useful clues to aid further investigation of these topics.

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中文摘要 自铁基化合物中发现高温超导电性以来,人们已经合成了众多具有不同间隔层的体系.同时科学家为揭示铁基超导体高温超导电性的特征和起源,在实验和理论研究方面都投入了大量的精力.但是直到今天其高温超导电性的起源仍然没有得以解决,特别是对正常态性质背后的物理还存在很多争论.本文总结了铁基超导体系的晶体结构以及相图,并提供了一些指向具有更高转变温度 T_c 的新超导体的提示和高温超导机理的线索.