TOPICAL REVIEW — Iron-based high temperature superconductors

Crystal chemistry and structural design of iron-based superconductors*

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The second class of high-temperature superconductors (HTSCs), iron-based pnictides and chalcogenides, necessarily contain Fe_2X_2 ("X" refers to a pnictogen or a chalcogen element) layers, just like the first class of HTSCs which possess the essential CuO_2 sheets. So far, dozens of iron-based HTSCs, classified into nine groups, have been discovered. In this article, the crystal-chemistry aspects of the known iron-based superconductors are reviewed and summarized by employing "hard and soft acids and bases (HSAB)" concept. Based on these understandings, we propose an alternative route to exploring new iron-based superconductors via rational structural design.

Keywords: iron-based superconductors, crystal chemistry, structural design

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1. Introduction

Since the discovery of superconductivity in the element mercury over a hundred years ago,[1] Numerous superconductors have been found continually in a diversity of materials. These superconductors can be classified into five groups, i.e., i) elements, ii) alloys or intermetallics, iii) inorganic compounds, iv) organic compounds, and v) polymers. Among them, the inorganic superconductors have been studied most extensively and intensively in recent decades, primarily because of the discovery of high temperature superconductivity in cuprates[2,3] and more recently in iron pnictides.[4,5]

While the nature of superconductivity was elucidated successfully over half a century ago in terms of Cooper pairing mediated by electron-phonon interactions,[6] the theory by itself supplies only limited guidance on exploring new superconductors, let alone for the exotic superconductors beyond the electron-phonon mechanism. Even if a material is theoretically designed and calculated to be a desirable superconductors (e.g., with higher superconducting transition temperature T_c), the proposed material must be thermodynamically or at least kinetically stable, such that it could be synthesized. The latter issue seems to be more crucial and challenging. Under this circumstance, the knowledge of crystal chemistry of a certain type of material is important and, it could be helpful to look for new superconductors. As a matter of fact, in the progress of finding new cuprate superconductors, the crystal chemistry has played an indispensable role.[7]

Iron-based superconductivity was first discovered in LaFePO in 2006 by Hosono H and co-workers.[8] The superconducting transition temperature T_c was only 3.2 K, which did not draw instant attentions from the community of superconductivity. Two years later, the same group reported superconductivity at 26 K in $LaFeAsO_{1-x}F_x$.[4] This breakthrough immediately aroused great research interests. Chen *et al.*[5] successfully pushed the T_c value beyond the McMillan limit by the substitution of Sm for La, marking the birth of the second HTSCs. The T_c record of ∼55 K was also created at the period.[9,10] In the following days of the year 2008, other three types of Fe-based superconductors (FeSCs) were found one after another.[11–13] So far, the iron-based HTSC family have included several dozen members. Although there have been a lot of reviews on the subject of iron-based superconductivity,[14–23] a complete classification and description for the crystal structures of FeSCs is still lacking. In this article, we present a comprehensive review on the crystal chemistry of FeSCs, aiming to explore new FeSCs in a rational way. We will not concentrate on the structural details, and the structural phase transitions are simply not touched. This related information can be found in Ref. [24].

2. Crystal chemistry

2.1. Chemical composition

Crystal chemistry seeks for the principles describing composition-structure-property relations in crystalline materials. Let us first discuss features of the chemical composition of FeSCs. Taken $LaFeAsO_{1-x}F_x$ (so-called "1111" material because it is a quaternary equiatomic compound) for example, the constituent elements (sequencing in the electronegativity order according to the standard nomenclature of inor-

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ganic compounds) La^{3+}, Fe^{2+}, As^{3-}, and O^{-} belong to different groups that are called hard acid, soft acid, soft base, and hard base, respectively, in the concept of "Hard and Soft Acids and Bases" (HSAB).[25] If we employ a notation *ADXZ* for the 1111 compounds, the characteristic of the constituent elements is well defined: *A* represents a "hard" (meaning non-polarizable) cation with the smallest electronegativity; *D* denotes a "soft" (meaning polarizable) cation (it is normally a *d*-block transition metal, but here it is virtually Fe for FeSCs); *X* represents a "soft" anion (e.g., a pnictogen or a chalcogen); *Z* is a "hard" anion with the largest electronegativity. According to the HSAB rule,[25] *A* tends to bond with *Z* (an ionic bonding), and *D* combines with *X* (covalent bonding dominated), as depicted in Fig. 1. The resultant two block layers A_2Z_2 and D_2X_2 are linked by *A*–*X* ionic bonding. As for other FeSCs, the HSAB concept basically holds. Therefore, we employ the $A_aD_dX_xZ_z$ (simplified as *adxz*) notation throughout this article.

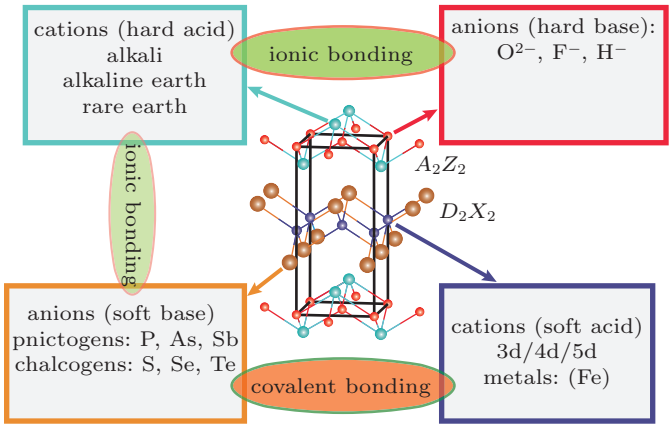


Fig. 1 Characteristic of the constituent elements and the chemical bonding in 1111-type *ADXZ* iron-based superconductors.

The combination of *ADXZ* leads to many members in the 1111 family. A review paper published in 2008 lists over 150 *ADXZ* individuals.[26] More 1111 compounds have been synthesized since 2008. However, the number of the iron-based compounds reported so far is only about 30. Importantly, the element-selective feature at the four crystallographic sites allows various kinds of successful chemical doping for inducing superconductivity. We will have more discussions on these issues in the following sections.

2.2. Fe_2X_2 layers represented by β-FeSe

Just like cuprate superconductors that possess the essential CuO_2 sheets, all the known FeSCs necessarily contain Fe_2X_2 ("*X*" refers to pnictogen or a chalcogen element) layers. The crystal structure of the Fe_2X_2 layers can be represented by β-FeSe [so-called "11" phase, see Fig. 2(a)] which itself is an FeSC ($T_c = 8$ K at ambient pressure).[13] (There was a confusion on the nomenclature in the literatures. FeSe with nearly 1:1 stoichiometry actually crystallizes in two polymorphs. One has a hexagonal NiAs-type structure, which is more stable than the tetragonal phase. Normally the former is called α-FeSe, and the latter is called β-FeSe.[27]) The β-FeSe crystallizes in a layered anti-PbO-type structure with space group $P4/nmm$. The Fe_2Se_2 monolayer consists of Fe_2 (two iron atoms in a unit cell) square-net sandwiched by two Se monolayers. In the language of the crystal chemistry, the Fe atoms are coordinated by four Se atoms, and the resulted $FeSe_4$ tetrahedra are edge-shared. In fact, the geometric configuration resembles that of Li_2O (with anti-CaF_2-type structure). That is the reason why literatures often refer the Fe_2X_2 layers to the anti-fluorite-type structure.

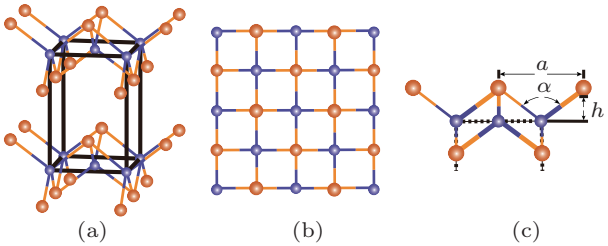


Fig. 2. (a) Crystal structure of β-FeSe which consists of infinite Fe_2Se_2 layers. (b) Top view along the *c*-axis direction. The structural parameters that are considered to be crucial to the superconducting transition temperature are marked in panel (c).

Then, what *X* can form stable Fe_2X_2 layers that incorporate with other structural blocks to have a high-temperature FeSC? Unfortunately, such *X* is limited to Se and As so far, although many efforts were made to explore possible superconductivity in an iron compound with other *X* such as Sb.[28–30]

Since the Fe_2X_2 layers are responsible for superconductivity, the structural details of the FeX_4 tetrahedra were considered to be a determinant factor controlling the T_c. Empirically, the relevant structural parameters are (i) the *a* axis,[31,32] (ii) the bond angle of $X-Fe-X$ (α),[33,34] and (iii) the height of *X* with respect to the Fe planes (h),[35] respectively. The latter two parameters have been widely cited because the maximum T_c in FeSCs seems to fall at $\alpha = 109.5°$ (corresponding to a right FeX_4 tetrahedron) and $h = 1.38$ Å. Theoretical calculations based on spin-fluctuation mechanism were able to elucidate the variations of T_c with the increase of h.[36] Nevertheless, overall T_c does not obey a unique relation to any of these parameters.[14] Perhaps, it is simply not suitable to consider the T_c values of all the FeSCs, irrespective of doping level, doping site, uniaxial pressures, or isotropic hydrostatic pressures. Besides, the two parameters α and h are not irrelevant. Therefore, the empirical relations have obvious flaws, which should be amended further.

Owing to the charge balance for satisfying Fe^{2+}, the 11-type (tetragonal polymorph) iron-containing compound must be a chalcogenide. Therefore, there are only three members: FeS, FeSe, and FeTe in the 11 family. These simple bi-

nary compounds were reported as early as in the 1930s.[37–39] Among them, FeTe is the most stable phase, and the crystals can be grown by a melting method.[40] The β-FeSe polymorph is not so stable. It was reported that annealing at lower temperatures was absolutely necessary to obtain a single phase.[41] The anti-PbO-type FeS is simply metastable, and it can be synthesized only through a soft chemical process in an aqueous solution.[42] The change in stability seems to be related to the criteria/rule of ionic radius ratio.[43] The ionic radius ratio between Fe^{2+} and S^{2-} does not satisfy the tetrahedral coordination well. If the average size of the X-site anions increases, the β-phase becomes stabilized. This is manifested by the fact that it is easy to synthesize the solid solutions of Fe(Te,Se)[44,45] and Fe(Te,S).[46] Interestingly, T_c can be enhanced up to about 14 K in both systems.

Apparently, the 11-type system is the simplest one among all FeSCs, however, here, we emphasize that the real crystalline status is much more complicated than one expected, primarily because some iron atoms (in the form of Fe^{2+}) occupy the interstitial site within the Van de Waals gap (X bilayers). Most importantly, such occupation suppresses superconductivity severely. It was reported that only 3% of the excess interstitial Fe completely destroyed the superconductivity in $Fe_{1.03}Se$.[47]

2.3. Other basic FeSC systems

By inserting a simple structural unit in between the Fe_2X_2 layers described above, some basic crystal structures can be derived as shown in Fig. 3. They are classified into four groups: namely, "111", "122", "122*"[15], and "1111" systems, according to the above $ADXZ$ notation, which is consistent with the common usage. The inserted units are a bilayer alkali and monolayer (or partially occupied) alkaline earth for the 111 and 122 (122*) structures, respectively. As for the 1111 structure, the R_2O_2 (R =rare earth) and $A_{E2}F_2$ (A_E = alkaline earth) "block layers" are intergrown into the Fe_2X_2 layers. Table 1 lists some representative FeSCs in the category of the five basic structures.

Table 1. Iron-based superconductors with five basic structures (11, 111, 122, 122*, and 1111). A general formula $A_aD_dX_xZ_z$ (see the text) is used to distinguish the type of elements that occupies/substitutes a certain crystallographic site. Representative chemical doping strategies are included. "HP" denotes the T_c measured under high pressures.

Structure/system	Chemical formula	T_c/K
11	FeSe	8[13]
DX	Fe(Se,Te)	14[44,45]
	FeSe	37 (HP)[48,49]
111	LiFeAs	18[12]
ADX	LiFeP	6[50]
	$Ba_{1-x}K_xFe_2As_2$	38[11]
122	KFe_2As_2	3.8[51]
AD_2X_2	$BaFe_2As_2$	29 (HP)[52]
	$BaFe_{2-x}Co_xAs_2$	25[53]
	$BaFe_2As_{2-x}P_x$	30[54]
122*	$K_{1-x}Fe_{2-y}Se_2$	32[55]
$A_{1-\delta}D_2X_2$	$(K,Tl)_{1-x}Fe_{2-y}Se_2$	31[56]
	$(K,Tl)_{1-x}Fe_{2-y}Se_2$	48 (HP)[a] [57]
	$LaFeAsO_{1-x}F_x$	26[4]
	$LaFeAsO_{1-x}F_x$	41 (HP)[58]
1111	$La_{1-x}Sr_xFeAsO$	25[59]
ADXZ	$RFeAsO_{1-x}$	40-55[31]
	$SmFeAsO_{1-x}F_x$	55[9]
	$Gd_{0.8}Th_{0.2}FeAsO$	56[10]
	$LaFe_{1-x}Co_xAsO$	14[60,61]
	$LaFeAs_{1-x}P_xO$	10.5[62]

[a]Another unknown superconducting phase at higher pressures.

The 111 phase crystallizes in an anti-PbFCl structure. Apparently, it differs much from the 11 phase, however, one may convert 11 to 111 continually by inserting alkali elements (Li or Na) into the X_5-pyramid interstitial site. Therefore, the space group is identical to that of β-FeSe. Members of the ADX family (with D = Fe) are relatively limited due to the confinements of charge balance and lattice match. Table 2 summarizes most of the 111-type iron compounds that have been synthesized.

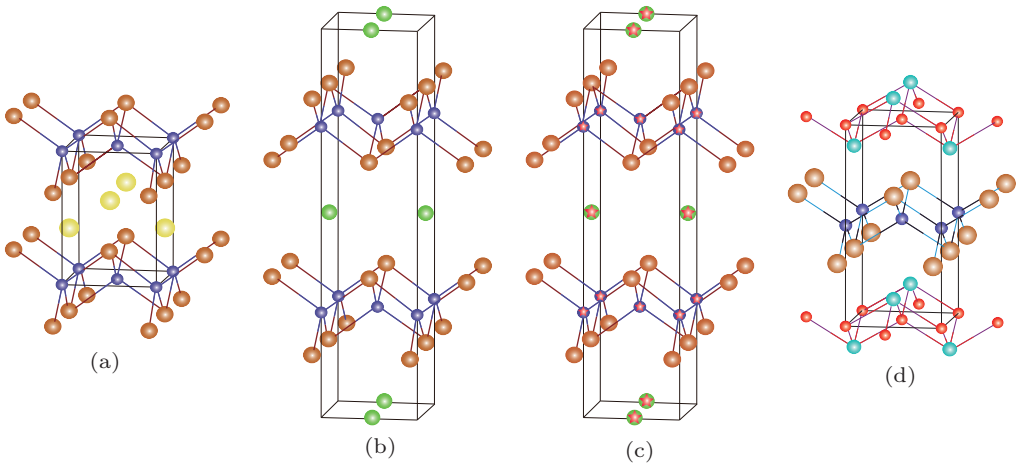


Fig. 3. Basic crystal structures of iron-based superconductors derived from the 11-type structure shown in Fig. 2. (a) 111-type ADX; (b) 122-type AD_2X_2; (c) 122*-type $A_{1-\delta}D_{2-\delta'}X_2$; (d) 1111-type $ADXZ$.

Table 2. Iron-containing 111-type compounds.

A/X[a]	P	As	Si	Ge
Li	LiFeP[50]	LiFeAs[64]	–	–
Na	–	NaFeAs[65]	–	–
Mg	–	–	–	MgFeGe[66,67]
R	–	–	RFeSi[b]	–

[a]CuFeSb also belongs to the 111 family. It is a rare iron antimide without obvious Fe deficiency. Ferromagnetism with a Curie temperature of 375 K was recently reported.[63]

[b]R = Y, Ce, La, etc.

It is noted that, among the compounds listed in Table 2, only the pnictides show superconductivity so far. LiFeP and LiFeAs become superconducting at 6 K and 18 K, respectively.[12,50] In fact, all the iron phosphides known have relatively low T_c. Nevertheless, it is not usual that the undoped LiFeAs shows superconductivity, because most undoped iron pnictides such as NaFeAs exhibit antiferromagnetic spin-density-wave transition.[14,15] The possible reason is that LiFeAs has a very small lattice ($a \sim 3.77$ Å). This implies that the "internal pressure" is at work, which leads to superconductivity by itself. Similar explanation might be valid for the appearance of superconductivity in β-FeSe. In comparison, the undoped NaFeAs shows complex magnetic transitions and, it is not superconducting without extrinsic doping. Superconductivity at 23 K appears when the sodium is significantly deficient.[65] By the Co doping and/or with applying high pressures, T_c can be increased up to 31 K, the record to our knowledge in the 111 system.[69,70]

The absence of superconductivity in the 111-type iron silicides and germanides[68] deserves further study. Although the Ge–Fe–Ge bond angle ($\alpha = 103.55°$) is far less than the ideal value, it is actually larger than that of LiFeAs ($\alpha = 102.79°$[71]). Therefore, some other factors such as electron correlation effect may also crucial for the appearance of superconductivity.

The 122 AD_2X_2 compounds have the $ThCr_2Si_2$-type structure with $I4/mmm$ space group. The A-site cations are coordinated by eight X atoms, thus the X–A–X triple-layer unit is analogous to CsCl-type block. Thus, this geometric configuration requires relatively large cations for A, as is true from Table 3. For the pnictides, A can be a larger alkali or alkaline earth elements. Eu is the exceptional rare earth that can form 122 ferroarsenides because Eu^{2+} is relatively stable and has relatively large size. The most interesting point for the Eu-containing 122 phases is that they may show anomalous superconducting and magnetic properties, which were called Fe-based ferromagnetic superconductors.[73–76] The researches along this line are worthy and expectable.

$ThCr_2Si_2$-type structure is widely adopted. A review paper in 1996 listed nearly 600 compounds of the type.[72] For the iron-based compounds, the number was much decreased. Even so, like the 111-type material, only the pnictides show superconductivity. The phosphides generally have very low T_c. For the arsenides, the T_c value depends on the doping level. In $Sr_{1-x}K_xFe_2As_2$ system, for example, the undoped $SrFe_2As_2$ is not superconducting. With the increase of the K substitution, T_c increases to a maximum value of 37 K at $x = 0.4$, and then T_c decreases steadily down to 3.8 K for $x = 1$.[51] In an electron-doped $Ca_{1-x}La_xFe_2As_2$ system, superconducting transition up to 49 K was observed.[77]

Table 3. Iron-containing 122 AFe_2X_2 compounds. The related references can be seen in a review article.[72] The review lists about 600 members in the $ThCr_2Si_2$-type family.

A/X	P	As	Si	Ge
K	KFe_2P_2	KFe_2As_2	–	–
Rb	$RbFe_2P_2$	$RbFe_2As_2$	–	–
Cs	$CsFe_2P_2$	$CsFe_2As_2$	–	–
Ca	$CaFe_2P_2$	$CaFe_2As_2$	–	–
Sr	$SrFe_2P_2$	$SrFe_2As_2$	–	–
Ba	$BaFe_2P_2$	$BaFe_2As_2$	–	–
Eu	$EuFe_2P_2$	$EuFe_2As_2$	$EuFe_2Si_2$	$EuFe_2Ge_2$
R	RFe_2P_2	–	RFe_2Si_2	RFe_2Ge_2

The AD_2X_2 compounds can be classified into two categories, depending on whether X–X is bonding or not.[78] For the compound with a small c/a ratio (~2.8), the X–X bonding is significant and, one often calls it a collapsed phase. It is interesting that no collapsed phase show high-temperature superconductivity, irrespective of chemical doping or applying pressures. This is probably related to the covalent X–X bonding, which greatly influences the electron correlations, the Fermi levels as well as the Fermi surface topology. Generally, the collapsed phase has a relatively large α angle, which does not favor high T_c superconductivity. Therefore, it is not surprising that the iron silicides and germanides do not show superconductivity at an elevated temperature.

There is another common structure type called $CaBe_2Ge_2$,[79] whose stoichiometry is also 1:2:2. It is also tetragonal, and contains anti-fluorite-like Be_2Ge_2 layers. The different structural feature is that there is a reverse arrangements for Be and Ge atoms, which forms Ge_2Be_2 layers that are linked with the "normal" Be_2Ge_2 block by Ca^{2+} cations. It was recently discovered that $SrPt_2As_2$, crystallized in the $CaBe_2Ge_2$-type structure, shows superconductivity at 5.2 K.[80] Unfortunately, it seems that the 4d and 5d elements tend to adopt this kind of structure, and no iron-based compounds with this structure has been reported so far.

At the end of 2010, Guo *et al.*[55] reported a 122-type ferroselenide superconductor $K_xFe_2Se_2$ with $T_c = 32$ K. While the average structure is the same as a normal $ThCr_2Si_2$, the cation deficiency, especially at the Fe-site,[56] makes the system special. So, it was called 122* phase by Stewart.[15] There have been a lot of studies along this line, primarily because it

has not only interesting superstructures but also complicated phase separations. For readers who are interested in the details, we recommend a recent review[81] which describes the main developments and the perspectives for this particular system.

Table 4. Iron-containing 1111 *ADXZ* compounds. Most of the related references can be seen in a review article.[26] The review lists over 150 members in the ZrCuSiAs-type family.

A–*Z*/*X*	P	As	Si
R[a]–O	*R*FePO	*R*FeAsO	–
Np–O	–	NpFeAsO[83]	–
Ca–F	–	CaFeAsF	–
Sr–F	–	SrFeAsF	–
Ba–F	–	BaFeAsF	–
Eu–F	–	EuFeAsF	–
Ce–H	–	–	CeFeSiH
Ca–H	–	CaFeAsH[84]	–

[a] R = La, Ce, Pr, Nd, Sm, Gd (synthesized at ambient pressure); More compounds with R = Tb, Dy, Ho, etc, were obtained by high-pressure synthesis technique.

The quaternary equiatomic compounds *ADXZ* have a tetragonal ZrCuSiAs-type structure ($P4/nmm$). As stated in the above section, the combination of *ADXZ* may produce many 1111-type compounds.[26] Nevertheless, the iron-based 1111 compounds are not so wealthy, as listed in Table 4. Here, we note that most of the ferro-oxyarsenides were synthesized by Quebe *et al.* in 2000.[82] If these compounds had been well studied in time, FeSCs would come out much earlier.

2.4. Extended FeSC systems: Intergrowth structures

2.4.1. Intergrowth with perovskite-like block layers

The a axis of the above FeSCs ranges from 3.77 Å to 4.03 Å, which makes $ABO_{3-\delta}$ perovskite-like layers compatible to form an intergrowth structure. As a matter of fact, similar intergrowth structures were reported earlier.[85–90] For example, the crystal structure of $Sr_2BO_2Cu_2S_2$ (B = Zn and Co) is an intergrowth of 122-type $SrCu_2S_2$ and oxygen-deficient perovskite-like $SrBO_2$ infinite layers.[85,86] Other intergrowth structures with thicker perovskite layers were also developed over a decade ago.[87,88] The homologous series can be written as $A_{n+1}B_nD_2X_2Z_{3n-1}$, whose crystal structures were shown in Fig. 4. The $n = 2$ structure consists of $A_3B_2Z_5$ block layers, and the $n = 3$ phase has more thicker of $A_4B_3Z_8$ building block. $Sr_3Fe_2Cu_2S_2O_5$[87] and $Sr_3Sc_2Cu_2S_2O_5$[89] belong to the $n = 2$ member, and $Sr_4Mn_3Cu_2S_2O_{8-\delta}$[88,90] is for the case of $n = 3$.

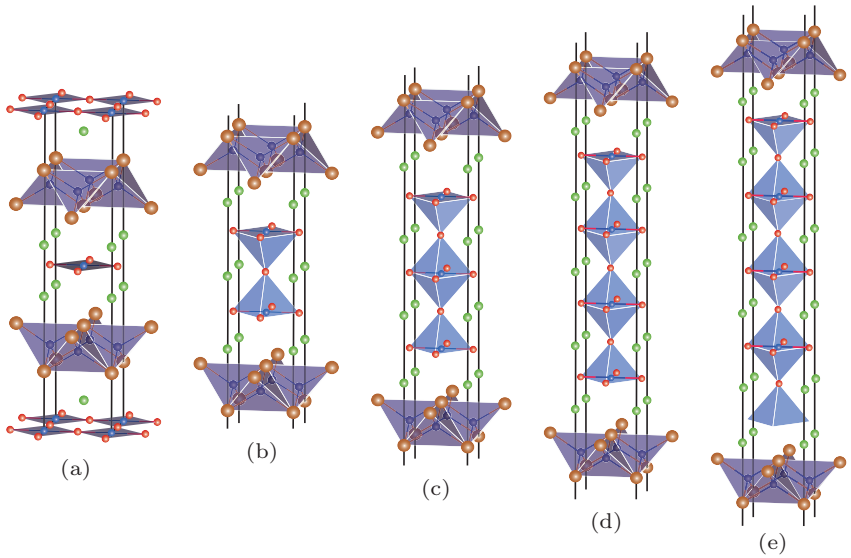


Fig. 4. Iron-based superconductors with intergrowth structures containing perovskite-like block layers. The general formula is $A_{n+1}B_nD_2X_2Z_{3n-1}$. The structures displayed from (a) to (e) correspond to $n = 1$ to 5.

The first reported compound with Fe_2As_2 and perovskite-like layers was 32225 (it was called 32522 in some literatures) ferroarsenide $Sr_3Sc_2Fe_2As_2O_5$,[91] an $n = 2$ member. Although the material does not show spin-density-wave anomaly, it was considered to host potential superconductivity. Indeed, traces of superconductivity at about 20 K were observed in the Ti-doped 32225 ferroarsenide.[92] Recently, the 32225 ferropnictides $Ca_3Al_2Fe_2X_2O_{5-\delta}$ (X = As and P), synthesized at high pressures, were reported to show superconductivity at 30.2 K and 16.6 K, respectively.[93] Other intergrowth structures with thicker perovskite block layers (n = 3, 4, 5) were also synthesized, and they all exhibit superconductivity.[94,95]

There was one special member of $n = 1$: $Sr_2CuO_2Fe_2As_2$ which comprises of superconductively-active Fe_2As_2 layers and CuO_2 sheets. Our first-principles calculations suggest a charge transfer from the Fe_2As_2 layers to the CuO_2 sheets.[96] Therefore, it is expected to show successive superconducting transitions in the two layers. Probably, many people tried to

synthesize this hypothetical object. The effort led to some related 21222 phase (with mixed occupations at B and D sites),[97] however, the target material has never been obtained. Very recently, $Sr_2CrFe_2As_2O_2$ was successfully synthesized, but unfortunately, the material was not superconducting down to 3 K.[98]

There is a perovskite derivative called Ruddlesden–Popper (RP) series $A_{n+1}B_nZ_{3n+1}$, which contain a rock-salt layer in addition to the perovskite layer.[100] Similarly, the oxygen-deficient RP layers can also be intergrown with the 122-type structure, forming another homologous series $A_{n+2}B_nD_2X_2Z_{3n}$. The crystal structures for $n = 2$, 3, and 4 are shown in Fig. 5.

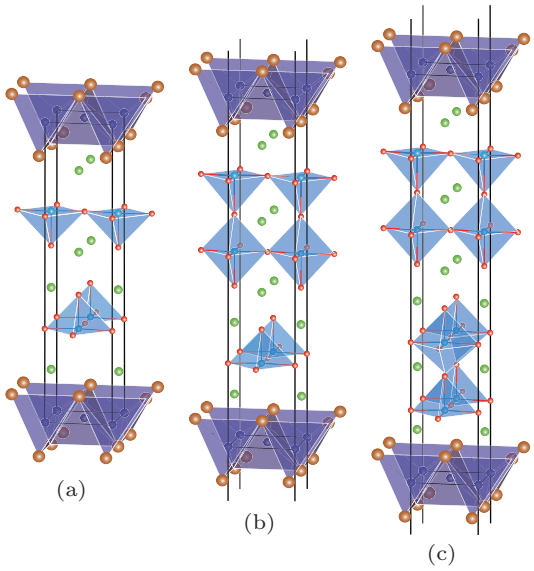


Fig. 5. Crystal structures of a homologous iron-based superconductors $A_{n+2}B_nD_2X_2Z_{3n}$ containing Ruddlesden–Popper block layers. Three members with (a) $n = 2$, (b) $n = 3$, and $n = 4$ have been synthesized.[99]

The pioneering example in this series was $Sr_2GaCuSO_3$ which consists of $Sr_3Ga_2O_6$ RP block and $SrCu_2S_2$ structural unit.[101] It was found that the 21113 (it was called 21311 or 42622 in some literatures) ferro-oxyphosphide $Sr_2ScFePO_3$ shows superconductivity at 17 K, the highest T_c in phosphides so far.[102] For the arsenides, $Sr_2VFeAsO_3$ exhibits superconductivity at 37.2 K without extrinsic doping or applying pressures.[103] The present author and co-workers explained it in terms of thte electronic self-doping due to a spontaneous charge transfer between the two building blocks.[104] In the cases of $B =$ Sc and Cr, the charge transfer is not obvious, thus they did not show superconducting transitions.[105,106] Partial substitution of Sc by Ti in $Sr_2ScFeAsO_3$ leads to superconductivity up to 45 K.[92]

In this homologous series, $n = 3$ and 4 members were also successfully obtained by Ogino *et al.*, with $A =$ Ca, $B =$ Al/Sc/Ti.[99] The $n = 4$ phase was well separated and characterized. Notably, the a-axis synthesized compounds are approximately 3.8 Å, close to those of FeSe and LiFeAs. Besides, the incorporation of Ti essentially induces excess electrons into the Fe_2As_2 layers. Thus, the series of new compounds exhibited bulk superconductivity with T_c up to 39 K.

2.4.2. Intergrowth with other exotic block layers

In addition to the perovskite-like layers, some "exotic" block layers were also able to be inserted into the Fe_2X_2 layers. In 2011, two platinum-containing compounds $Ca_{10}Pt_3As_8(Fe_2As_2)_5$ and $Ca_{10}Pt_4As_8(Fe_2As_2)_5$, called 10–3–8 and 10–4–8 phases respectively, were reported.[107] The crystal structures (Fig. 6) are not so complicated as the formula suggests. The Fe_2As_2 layers are virtually intact, which makes it possible to become superconducting through a chemical doping. The intermediate part is a little complex. The Pt atoms are square-coordinated, and resultant $PtAs_4$ squares are linked by sharing the vertex. The 2×2 superlattice of Pt (i.e., Pt_4As_8) happens to match the $\sqrt{5}\times\sqrt{5}$ superlattice of Fe_2As_2, forming 10–4–8 structure. In the intermediate layer of the 10–3–8 phase, one of the four Pt sites is absent, leaving the Pt_3As_8 planes between Fe_2As_2 layers.

Through partial substitution of Pt for Fe in the Fe_2As_2 layers, superconductivity at 11 K and 26 K were observed in the 10–3–8 and 10–4–8 phases, respectively.[107] The difference in T_c for these similar compounds with a similar As–Fe–As bond angle challenges the empirical rule and, it was suggested that the interlayer coupling plays an important role in enhancing T_c in the FeSCs.

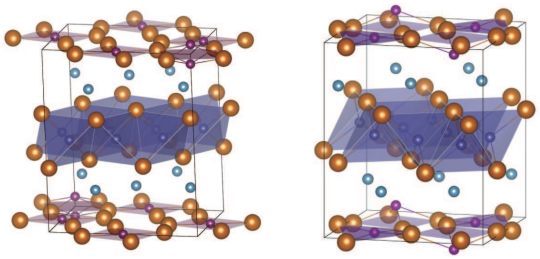


Fig. 6. Crystal structures of iron-based superconductors containing intermediate layers of Pt_3As_8 and Pt_4As_8 (based on a $\sqrt{5}\times\sqrt{5}$ superlattice in Fe_2As_2 layers): (a) $Ca_{10}Pt_3As_8(Fe_2As_2)_5$, and (b) $Ca_{10}Pt_4As_8(Fe_2As_2)_5$.

We noted that a class of titanium oxypnictides contains the Ti_2O square lattice,[108] which well matches Fe_2As_2 layers. The interesting issue of the titanium oxypnictides lies in a density-wave (DW) anomaly that is related to the Ti_2O sheets. In 2010, a relatively simple titanium oxypnictide $BaTi_2As_2O$ was prepared and characterized, which shows a DW anomaly at 200 K.[109] We then considered to incorporate the Ti_2O sheets into the Fe_2As_2 layers. After some attempts, we finally succeeded in synthesizing the intergrowth structure of

$BaTi_2As_2O$ and $BaFe_2As_2$,[110] as shown in Fig. 7. Bulk superconductivity at 21 K was observed after the sample annealing without apparent doping. In addition, a DW anomaly appears at $T_{DW} = 125$ K, which is remarkably lower than that of $BaTi_2As_2O$. By first-principless calculations, these phenomena were attributed to a self doping due to the charge transfer from the Ti_2O sheets to the Fe_2As_2 layers.[111] Further physical property investigations are under way.

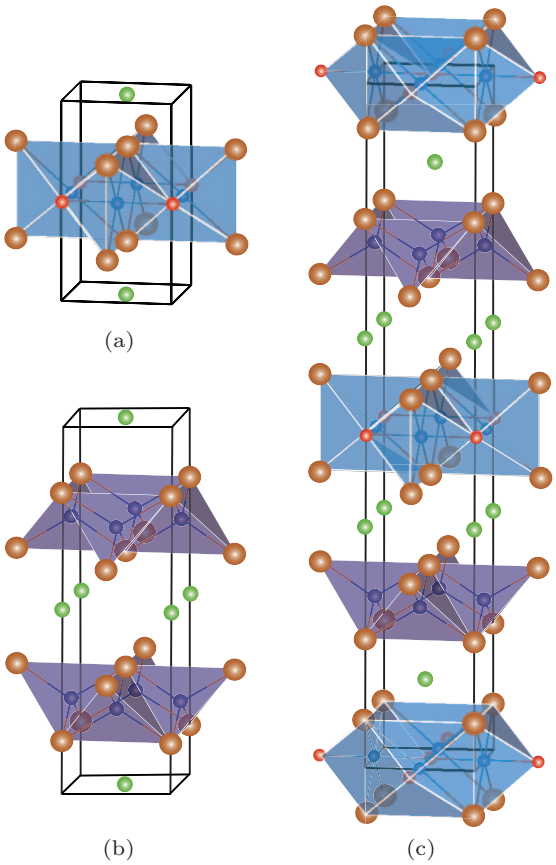


Fig. 7. Intergrowth of $BaTi_2As_2O$ (a) and $BaFe_2As_2$ (b) produces a new iron-based superconductors $Ba_2Ti_2Fe_4As_4O$. (c) Note that the Ti_2As_2O layers are also conducting, making the material distinct from other FeSCs.

Table 5. Four groups of "extended" iron-based superconductors containing relatively thick intermediate layers.

Structure/system	Chemical formula	$T_{c,max}$/K
	$A_{n+1}B_nD_2X_2Z_{3n-1}$	
32225 ($n = 2$)	$Sr_3(Sc,Ti)_2Fe_2As_2O_5$	20[92]
32225 ($n = 2$)	$Ca_3Al_2Fe_2As_2O_5$	30.2[93]
43228 ($n = 3$)	$Ca_4(Sc,Ti)_3Fe_2As_2O_8$	47[94]
542211 ($n = 4$)	$Ca_5(Sc,Ti)_4Fe_2As_2O_{11}$	46[95]
652214 ($n = 5$)	$Ca_6(Sc,Ti)_5Fe_2As_2O_{14}$	42[95]
	$A_{n+2}B_nD_2X_2Z_{3n}$	
21113 ($n = 2$)	$Sr_2ScFePO_3$	17[102]
21113 ($n = 2$)	$Sr_2VFeAsO_3$	37.2[103]
32116 ($n = 4$)	$Ca_3(Al,Ti)_2FeAsO_6$	39[99]
10–3–8	$Ca_{10}Pt_3As_8(Fe_2As_2)_5$	11[107]
10–4–8	$Ca_{10}Pt_4As_8(Fe_2As_2)_5$	26[107]
22241	$Ba_2Ti_2Fe_2As_4O$	21[110]

Table 5 summarizes the extended four types of FeSCs with relatively thick intermediate layers. The optimal T_c values seem to be independent of the type of intermediate layers. Although the empirical rule for T_c is basically obeyed, here, we emphasize that the possible mixed occupations in the B/D site may greatly influence the maximum T_c. In this regard, the simpler 1111 system has the advantage avoiding such mutual occupations, and therefore, it exhibits the highest T_c among FeSCs.

2.5. Superconductivity induced by chemical doping

Most FeSCs are realized by a certain chemical doping, although there are few exceptions (e.g., β-FeSe and LiFeAs). The parent compounds are generally an antiferromagnetic spin-density-wave (SDW) bad metal. By chemical doping, the SDW ordering is suppressed, and then superconductivity emerges. For different systems and/or different doping strategies, the detail of the superconducting phase diagram varies to some extent, but the generic tendency keeps unchanged.[14,15,20,21] It is widely believed that such generic phase diagram holds even for other exotic superconductors including high T_c cuprates, high T_c pnictides and chalcogenides, heavy Fermion superconductors, and organic superconductors.

However, the parent compounds of FeSCs seem to be most close to the superconducting ground state, because various doping (being viewed as a perturbation), even applying a moderate pressure, can induce superconductivity. Table 6 summarizes the representative chemical doping strategies that have been widely employed. Several points can be drawn from the table. (i) Chemical doping at any crystallographic site is effective to induce superconductivity. Of particularly surprising is that the doping (even up to 50%) within Fe_2As_2 layers does not destroy superconductivity. (ii) Superconductivity is able to be introduced by either the electron doping, the hole doping, or the non-charge-carrier (so-called isoelectronic) doping. (iii) Superconductivity can be observed without doping. In this category, we believe that either internal charge transfer (self-doping[104,111]) or internal pressure is at work. (iv) Overall speaking, the electron doping is easier to obtain superconductivity. For detailed information to the chemical doping study, a featured review (in Chinese) can be referred.[113]

Table 6 also indicates that, in some cases, the chemical doping is not successful to generate superconductivity. One reason is that the doping limit (or the substitution solubility) is too small to turn superconductivity on. The other reason for the absence of superconductivity is that, the doping fails to supply sufficient perturbations to push the system to superconducting ground state, or the dopant itself kills the potential superconductivity. For example, the isoelectronic doping at A site may also supply chemical pressure (CP), but it is not successful to induce superconductivity. We explain this phenomenon as follows. In a multielement system, the CP may be "inhomogeneous", as was demonstrated by a systematic study

on (R, Pr)$Ba_2Cu_3O_y$-related system.[114–116] In iron pnictides, the CP by A-site doping does not supply enough internal pressure onto the Fe_2X_2 layers (although the lattice constants a and c both decrease). That is the possible reason why the CP by the doping away from the Fe_2X_2 layers cannot produce superconductivity.

Table 6. Classification of chemical doping that induces Fe-based superconductivity in a A–B–D–X–Z (see text for the notations) system.

Site/Type	Electron	Hole	Isoelectronic
A	Th^{4+}/R^{3+} [10]	A^{+}/A_E^{2+} [11]	not successful
B	Ti^{4+}/Sc^{3+} [92]	not successful	not successful
D	Co/Fe[60,61]	not successful	Ru/Fe[112]
X	not successful	not successful	P/As[54]
Z	F^{-}, H^{-}/O^{2-} [4]	not successful	not successful
Z	O vacancy[4]	not successful	not successful

3. Structural design

3.1. Principles of structural design

Since all the known FeSCs contain Fe_2X_2 layers, new FeSCs can be explored by a rational structural design. The structural building is something like a "lattice stacking engineering" (LSE). Fortunately, the LSE for FeSCs is relatively simple because it is confined to the stacking along the c axis in order to be compatible with the infinite Fe_2As_2 layers. In practice, it is our aim to find a distinct block layer between the Fe_2X_2 layers, and the designed object must be ultimately synthesized.

Here, we propose some points that should be taken into consideration for a structural design.

I) **Laws of crystal chemistry** In general, the law of crystal chemistry[43] should be referred as a guidance. For example, the radius ratio rule is particularly effective for an ionic bonding.

II) **Lattice match** Perhaps the first condition for a successful LSE is that the building block should basically match the essential Fe_2X_2 lattice. In this respect, Fe_2X_2 layers have very good compatibility because the a axis varies from ~3.75 Å to ~4.10 Å. Therefore, many crystallographic layers like CaF_2-type, CsCl-type, NaCl-type, and perovskite-like blocks can be employed as candidates for the building unit.

III) **Charge balance** The next important issue to be considered is charge balance. Empirically, the most stable valence state of Fe in pnictides or chalcogenides is 2+. This means that the Fe_2Pn_2 (Pn represents a pnictogen) unit carries charges $+2e$ such that the intermediate block must bring approximate $-2e$ to neutralize the system. This is the case that most FeSCs obey. The non-charged Fe_2Ch_2 (Ch denotes a chalcogen) layers in the chalcogenides makes it not so compatible for an ionic interlayer bonding. For the collapsed 122 block, there is interlayer covalent bonding, thus, the change of the valence state of X should be considered.

IV) **Rule of HSAB** The HSAB concept can be very useful in designing a multielement compounds. With the classification of the different type of elements in the HSAB scheme, one may easily find a suitable element for a specific site.

V) **Self-stability** Your designed compound must be at least apparently stable by itself. Mixed occupations should be avoid as far as possible. Make sure that "internal redox reaction" will not take place in the chemical formula designed.

3.2. Examples of structural design

In this subsection, we present some examples of structural design for FeSCs. One should recognize that the proposed structures are not successful unless they are ultimately synthesized. On the other hand, it is very difficult to rule out the possiblity of realization of a certain structure, because there are lots of possible combinations of the constituent elements and, the synthetic methods and conditions are not limited. We wish the readers would find that some of the examples here could be useful and illuminating.

Figure 8 displays some simple structures. Structure (a) is derived by adding another fluorite-type layer on the 1111 phase. The general formula is $A_3Fe_2X_2Z_4$. Such thick fluorite-type layers are very common in the cuprate superconductors.[17] In addition, there is an example of the similar building block in $Eu_3F_4S_2$.[117] Therefore, this structure could be synthesized if we chose the correct compositions and with suitable synthetic techniques (perhaps high-pressure method should be employed).

By adding a CsCl-type AX' layer into the 122 phase, the structure of Fig. 8(b) with a formula of $A_2Fe_2X_2X'$ can be obtained. One should pay attention to the charge valence for this structure. Figure 8(c) shows an example that the A-site ions are ordered because of the difference in valence states or ionic sizes. It is actually a superstructure (along the c axis) of 122 phase. A possible candidate is $KLaFe_4As_4$. Although our preliminary attempt failed, it could be successful by a low-temperature synthesis which tends to favor an ordered phase.

Up to now, the record T_c of FeSCs appears in 1111 system. Therefore, a 1111-like structure would be promising for an elevated T_c. If the Z-site ion of the 1111 phase is too large to adopt the fluorite configuration, a distorted 1111 structure would form. This case is shown in Fig. 8(d). The intermediate layer is analogous to the Van de Waals gap of PbFCl. Thus, AFeAsCl (A = Ca, Cd, Pb) could be candidates of this type structure.

It seems to be true that the Fe_2X_2-based materials have a T_c limit of ~ 60 K. To explore opportunities of higher T_c in FeSCs, one may consider modifying the Fe_2X_2 layers. Figure 8(e) shows an example of this attempt. It contains a thick superconductively-active Fe_4As_3 layers. If such a material came out, higher T_c could be expectable. It is noted here that the same structure already exists (e.g., KCu_4S_3[118]).

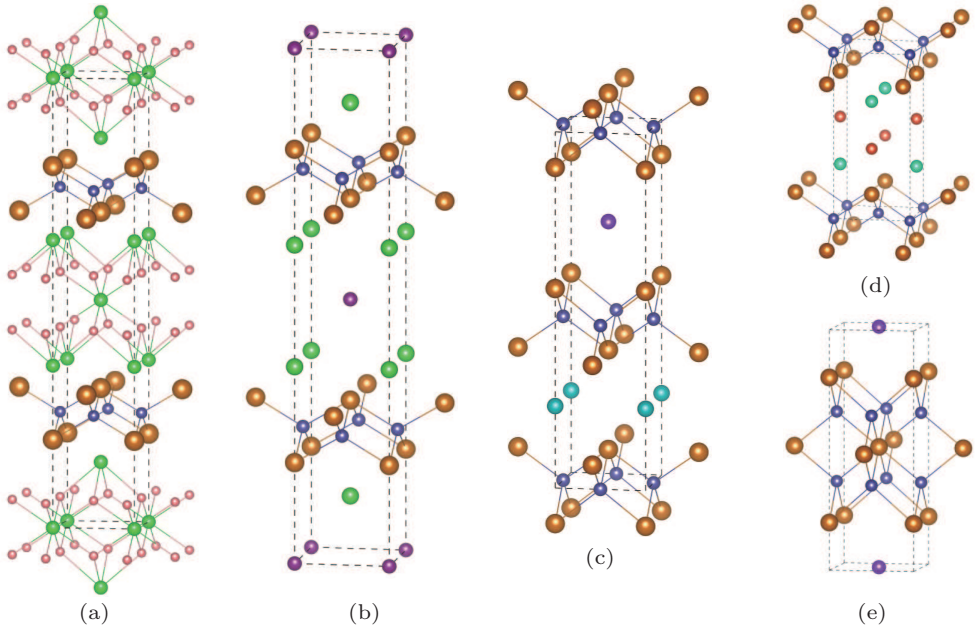


Fig. 8. Examples of structural design for FeSCs. (a) $A_3Fe_2X_2Z_4$; (b) $A_2Fe_2X_2X'$; (c) $KLaFe_4As_4$; (d) $AFeAsCl$; (e) AFe_4As_3.

The structures shown in Fig. 9 are constructed by more building blocks. The very left structure is an intergrowth of 122 and 1111. The resultant chemical formula is $A_3Fe_4X_4Z_2$. A nickel-based material crystallizes in the same structure, which shows superconductivity at 2.2 K.[119]

In Fig. 9(b), a thick A_4BZ_6 block layer, which consists of A_2BZ_4 and A_2Z_2 layers, is sandwiched into the Fe_2X_2 layers. The general chemical formula is $A_4BFe_2X_2Z_6$. Figure 9(c) shows a composite structure containing Fe_2X_2, perovskite-like $A_3B_2Z_5$ and anti-perovskite B_2X_2Z layers. The general chemical formula is $A_5B_4Fe_4X_4Z_7$.

The last structure we recommend contains a building block Bi_2S_4 which was recently found as a new superconductively-active layers.[120] In this proposed structure, a fluorite-type A_2Z_2 layers are present. It can also be viewed as an intergrowth of $LaBiS_2O$ and 1111 structure. A possible candidate is $(La,Sr)_2InFeSe_3O_2$, after considering the lattice match and the charge balance.

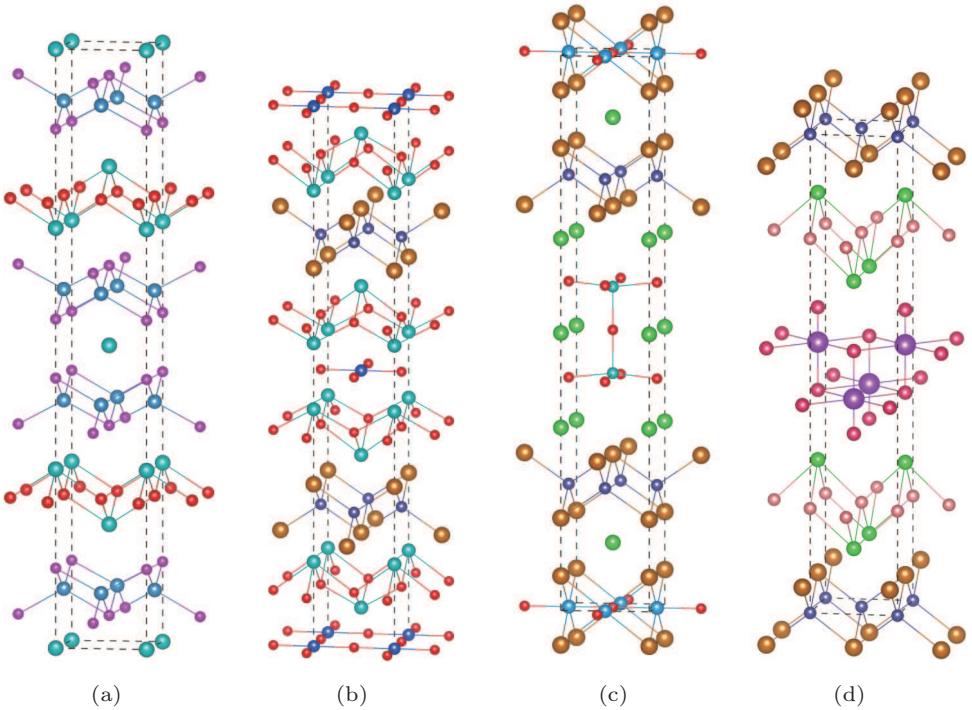


Fig. 9. More examples of structural design for FeSCs. (a) $A_3Fe_4X_4Z_2$; (b) $A_4BFe_2X_2Z_6$; (c) $A_5B_4Fe_4X_4Z_7$; (d) $(La, Sr)_2InFeSe_3O_2$.

To be honest, most designed objects are not likely to be successful. Thus, the evaluation of the stability of a designed material is very crucial. In this respect, first-principles calculations would be helpful under certain circumstances. We hope to develop this kind of skills soon, in order to make the structural design more rational.

4. Summary and outlook

In summary, the crystal chemistry of FeSCs bears some common characteristics such that a structural design for new FeSCs is possible. All the known FeSCs possess anti-fluorite-type Fe_2X_2 layers, which are believed to be responsible for superconductivity. Other elements in a certain FeSC help to form a three-dimensional lattice, and also assist to tune the superconductivity to an optimal level.

There have been some dozens of FeSCs discovered so far, classified into nine groups as listed in Table 1 and Table 5. The superconducting transition temperature T_c scatters from ~10 K to ~55 K, somewhat depending on the structural parameters such as the bond angle of X–Fe–X and the height of X with respect to the Fe-plane. In fact, the maximum T_c also depends on the type of doping. In general, the doping on the Fe_2X_2 layers (especially at the Fe site) inevitably brings disorder effect, which could suppress T_c to some extent.

By employing the HSAB concept, it is more clear that a specific crystallographic site in an FeSC belongs to a certain group of elements. Based on this point, we have summarized the members of iron-containing compounds for the major type of materials (Table 2 to Table 4). We have also summarized different kinds of chemical doping that may induce superconductivity (Table 6). These knowledge should be useful for selecting a chemical dopant and designing a new structure.

Five years have passed since the breakthrough of FeSCs in the Spring of 2008. The number of new FeSCs discovered seems to decay rapidly with time. Therefore, maybe we need a rational route in combination with a systematic study. We have proposed nine structures in this paper. We hope that they could be synthesized at some time in the near future.

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