Structural chemistry of superconducting pnictides and pnictide oxides with layered structures

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Abstract. The basic structural chemistry of superconducting pnictides and pnictide oxides is reviewed. Crystal chemical details of selected compounds and group subgroup schemes are discussed with respect to phase transitions upon charge-density formation, the ordering of vacancies, or the ordered displacements of oxygen atoms. Furthermore, the influences of doping and solid solutions on the valence electron concentration are discussed in order to highlight the structural and electronic flexibility of these materials.

Introduction

Among the huge number of ternary \(A_1T_1Pn_1, AE_1T_1Pn_1\), and \(RE_1T_1Pn_1\) pnictides (\(A\) = alkali metal, \(AE\) = alkaline earth metal, \(RE\) = rare earth metal, \(T\) = late transition metal, \(Pn\) = P, As, Sb, Bi) those with the compositions \(1:1:1\) and \(1:2:2\) have most intensively been studied in the past 30 years. Especially the rare earth containing compounds exhibit interesting magnetic and electrical properties. These classes of compounds have repeatedly been reviewed in book chapters of the Handbook on the Physics and Chemistry of Rare Earths.

Most of the \(1:2:2\) compounds crystallize with the tetragonal ThCr\(_2\)Si\(_2\) type structure \([1]\), space group \(I4/mmm\), a ternary ordered version of the BaAl\(_4\) type \([2]\). A broader diversity of structure types is observed for the \(1:1:1\) compounds. Only few of them adopt the tetragonal PbFCl type \([3]\). The basic crystallographic data of all these intermetallics are summarized in the Pearson Handbook \([4]\).

The PbFCl structure type leaves some empty tetrahedral voids that might be filled, leading either to a ternary compound of composition \(1:1:2\) (HfCuSi\(_2\)) or to a quaternary one of composition \(1:1:1:1\), first determined for ZrCuSiAs \([5]\). So far, there are only few examples, where a reversible filling of such voids occurs. This is the case for hydride formation of CeRuSi \(\rightarrow\) CeRuSiH \([6]\) and CeRuGe \(\rightarrow\) CeRuGeH \([7]\). The crystal chemical data of the huge number of ZrCuSiAs materials have recently been reviewed \([8]\).

Although the basic crystallographic data of the many ThCr\(_2\)Si\(_2\) and ZrCuSiAs type compounds are known for several years, especially for the ZrCuSiAs family, systematic property studies have been performed only recently. These investigations mainly focused on \(p\)-type transparent semiconductors like LaCuSO (for a review see \([9]\)) or the colored phosphate and arsenide oxides \(REZnPO\) \([10]\) and \(REZnAsO\) \([11]\).

The class of ZrCuSiAs type compounds gained a true renaissance in 2006, when superconductivity was reported for LaFePO \([12–14]\) and LaNiPO \([15, 16]\), however, at comparatively low transition temperatures of 3.2 and 4.3 K. Shortly later, a much higher transition temperature of 26 K was observed for LaFeAsO\(_1\_x\)F\(_x\) \([17]\), and even 55 K was determined for SmFeAsO\(_1\_x\)F\(_x\) \([18]\). Fluorine doping on the oxygen sites suppresses the spin-density-wave formation, favoring superconductivity.

In the ThCr\(_2\)Si\(_2\) family only few superconducting compounds, i.e. LaIr\(_2\)Ge\(_2\), LaRu\(_2\)P\(_2\), YIr\(_2\)_2S\(_2\), and BaNi\(_2\)P\(_2\) with low transition temperatures have been reported \([19–22]\). Also this field grew rapidly, when superconductivity with a maximum transition temperature of 38 K has been observed for the solid solution Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) \([23, 24]\). Again, potassium doping destroys the antiferromagnetic ordering of the iron substructure of BaFe\(_2\)As\(_2\) \([25]\) and leads to superconductivity.

These two discoveries led to a tremendous output since 2008 in various fields: (i) searching for new compounds, (ii) systematic doping experiments for property variations, (iii) systematic physical property studies, and (iv) theoretical investigations for a deeper understanding of the structure-property relationships and the mechanisms of superconductivity.

Although this period is still quite short, already diverse reviews on this highly exciting field have been published \([26–34]\) and special issues in New Journal of Physics \([35]\) and Physica C: Superconductivity \([36]\) have been edited. The vast numbers of physical property measurements have competently been reviewed by Johnston \([37]\).
Herein we focus on diverse structure chemical aspects of such superconducting pnictides and pnictide oxides with a stronger emphasis on stacking variants (intergrowth structures) and group-subgroup relations.

**Basic crystal structures**

The basic building unit of the various ternary pnictide and pnictide oxide crystal structures are layers of $TPn_{44}$ tetrahedra. As emphasized in Fig. 1, these $TPn_{44}$ tetrahedra share four common edges and the tetrahedra keep $4m2$ site symmetry. These tetrahedral layers are separated and charge balanced either by $A^+$, $AE^{2+}$, or $RE^{3+}$ cations, by $[REO]^{1-}$ layers, or by perovskite-related oxydic slabs.

In Fig. 2 we present the structures of LiFeAs [38, 39], LaFeAsO [40, 41], and BaFe$_2$As$_2$ [25, 42]. The basic crystallographic data of these arsenides and related pnictides are listed in Table 1. The three tetragonal structures have similar negatively charged layers of Fe$_{44}$ tetrahedra. In LiFeAs and LaFeAsO these layers are well separated by double layers of lithium atoms, respectively the positively charged [LaO]$^-$ layers. This is different in BaFe$_2$As$_2$. Here we observe large cages of coordination number 16 which are filled by the barium atoms. The double layers of Li$^+$ also lead to a different packing of the layers as compared to BaFe$_2$As$_2$.

The Fe–As distances in the three structures vary between 240 and 241 pm, close to the sum of the covalent radii of 237 pm [43], indicating substantial covalent Fe–As bonding, in agreement with diverse electronic structure calculations carried out on these materials. Furthermore one observes weaker Fe–Fe bonding within the tetrahedral layers. The Fe–Fe distances of 267 (LiFeAs), 280 (BaFe$_2$As$_2$), and 285 (LaFeAsO) pm are longer than those of 248 pm in α-Fe [44]. The weak Fe–Fe bonding was substantiated by electronic structure calculations.

The structure of NdZnPO [45] shows a different tetrahedral layer. As compared to the many tetragonal ZrCuSiAs type phases, the ZnP$_{44}$ tetrahedra in rhombohedral NdZnPO only share three common edges (Fig. 1) and they exhibit site symmetry $3m$. These tetrahedral double layers are then alternately stacked with ONd$_{44}$ tetrahedra in a rhombohedral fashion (Fig. 3). So far, this peculiar structure type has only been observed in quaternary zinc phosphide oxides. CeZnPO and PrZnPO are dimorphic [46]. The high-temperature (β) NdZnPO type modifications were obtained at 1170 K while the low-temperature (α) ZrCuSiAs type modifications crystallizes at 970 K.

The four structure types discussed above have many representatives. The basic crystallographic data are summarized in Refs. [8] and [37]. Besides these more or less simple structures, where the [FeAs]$^{3+}$ layers are separated just by the cations or the $[REO]^{1-}$ layers, a variety of stacking variants have recently been reported, where the [FeAs]$^{3+}$ layers show larger separation through insulating oxide slabs. The crystal chemical features of these compounds are discussed in the following paragraph.

The first reported compound with Fe$_2$As$_2$ layers separated by thick perovskite-like oxide blocks was Sr$_3$Sc$_2$O$_{5}$Fe$_2$As$_2$ [47]. This was derived from the known sulfide-oxide Sr$_3$Sc$_2$Cu$_2$S$_2$ [48], which crystallizes with the Sr$_3$Fe$_2$O$_5$Cu$_2$S$_2$-type structure in the space group $Ihmmmm$ [49]. At that time, the latter compounds were considered as candidates for new oxide superconductors. Figure 4a shows the crystal structure, where Fe$_2$As$_2$ layers and perovskite-like Sr$_3$Sc$_2$O$_5$ (SrScO$_2$/SrO/SrO/Cu) layers are stacked along the c axis. Scandium has five oxygen neighbors forming square ScO$_{4}$/O$_{1/2}$ pyramids, which share the apical oxygen atom. The distance to the arsenic atom is 339 pm. This is not a significant bond, since typical Sc-As distances are around 270 pm and the sum of the van-
superconductivity could be detected in Sr$_3$Sc$_2$O$_5$Fe$_2$As$_2$. Neither magnetic ordering nor any structural anomaly or anomalies was observed in this compound. These results provide evidence for the lack of crucial properties in Sr$_3$Sc$_2$O$_5$Fe$_2$As$_2$.

Table 1. Basic crystallographic data of selected ternary pnictides and pnictide oxides with layered structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>space group</th>
<th>(a) (pm)</th>
<th>(c) (pm)</th>
<th>(V) (nm$^3$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFeAs</td>
<td>P4\overline{mmm}</td>
<td>377.360(4)</td>
<td>635.679(1)</td>
<td>0.0907</td>
<td>[39]</td>
</tr>
<tr>
<td>LaFeAsO</td>
<td>P4\overline{mmm}</td>
<td>432.268(1)</td>
<td>874.111(4)</td>
<td>0.1422</td>
<td>[41]</td>
</tr>
<tr>
<td>BaFeAs$_{1/2}$</td>
<td>I4\overline{mmm}</td>
<td>396.25(1)</td>
<td>1301.68(3)</td>
<td>0.2044</td>
<td>[25]</td>
</tr>
<tr>
<td>Sr$_2$ScO$_3$F</td>
<td>I4\overline{mmm}</td>
<td>406.9</td>
<td>2687.6</td>
<td>0.4450</td>
<td>[47]</td>
</tr>
<tr>
<td>Sr$_2$Sc$_2$O$_4$F$\beta$</td>
<td>P4$\overline{mmm}$</td>
<td>401.6</td>
<td>1554.3</td>
<td>0.2507</td>
<td>[58]</td>
</tr>
<tr>
<td>Sr$_2$VO$_3$FAs</td>
<td>P4\overline{mmm}</td>
<td>392.96</td>
<td>1567.32</td>
<td>0.2420</td>
<td>[61]</td>
</tr>
<tr>
<td>Sr$_3$Cr$_2$O$_6$FAs</td>
<td>P4\overline{mmm}</td>
<td>391.12(1)</td>
<td>1579.05(3)</td>
<td>0.2416</td>
<td>[51]</td>
</tr>
<tr>
<td>Na$_2$Ti$_2$AsO</td>
<td>I4\overline{mmm}</td>
<td>407.0(2)</td>
<td>1528.8(4)</td>
<td>0.2532</td>
<td>[70]</td>
</tr>
<tr>
<td>BaTi$_2$As$_2$O</td>
<td>P4\overline{mmm}</td>
<td>404.7(3)</td>
<td>727.5(4)</td>
<td>0.1192</td>
<td>[72]</td>
</tr>
<tr>
<td>(SrF)$_2$Ti$_2$As$_2$O</td>
<td>I4\overline{mmm}</td>
<td>404.865(5)</td>
<td>1942.04(2)</td>
<td>0.3183</td>
<td>[73]</td>
</tr>
<tr>
<td>Sr$_2$Mn$_2$CuAs$_2$O$_2$</td>
<td>I4\overline{mmm}</td>
<td>407.913(6)</td>
<td>1858.26(3)</td>
<td>0.3092</td>
<td>[76]</td>
</tr>
<tr>
<td>Nd$_2$Fe$_2$Sc$_2$O$_5$</td>
<td>I4\overline{mmm}</td>
<td>402.63(1)</td>
<td>1843.06(2)</td>
<td>0.2988</td>
<td>[79]</td>
</tr>
<tr>
<td>La$_5$Cu$_3$As$_4$O$_8$Cl$_2$</td>
<td>I4\overline{mmm}</td>
<td>413.46(7)</td>
<td>4144(1)</td>
<td>0.7084</td>
<td>[80]</td>
</tr>
</tbody>
</table>

The closely related compounds $A_2MO_3$Fe$Pn$ ($A=$ Ca, Sr, Ba; $M=$ Sc, Cr, V; $Pn=$ As, P) [57–59] crystallize with the Sr$_2$GaO$_3$CuS-type structure [60] in the space group $P4\overline{4}$mm, shown in Fig. 4b. The distance between the Fe$_2$P$_{1/2}$ layers is about 1500 pm separated by perovskite-like blocks made of two MO$_{4/2}$O sheets without connection via the apical oxygen atoms, in contrast to Sr$_3$Sc$_2$O$_4$Fe$_2$As$_2$. Sr$_2$Sc$_2$O$_4$FeP is superconducting below 17 K [58], which is the highest $T_c$ in iron phosphides so far. Interestingly, among the series Sr$_2$MO$_3$FeAs ($M=$ V, Sc, Cr), only the undoped vanadium compound Sr$_2$VO$_3$FeAs exhibits bulk superconductivity at $T_c = 37$ K [61], which increases to 45 K under pressure [62]. None of them shows magnetic ordering of the iron substructure or any kind of structural distortion at low temperatures. Neutron diffraction experiments with Sr$_2$CrO$_3$FeAs revealed antiferromagnetic ordering of the chromium atoms and an intrinsic doping of about 7% chromium into the iron layer [63]. This may be a reason for the absence of superconductivity, because Cr-doping has proven to be poisonous to superconductivity in 122-type iron arsenides [64]. On the other hand, it is still unclear why superconductivity emerges in stoichiometric Sr$_2$VO$_3$FeAs, but not in Sr$_2$Sc$_2$O$_4$FeAs. A self-doping effect through $V^{3+}/V^{4+}$ mixed valence has been suggested from X-ray absorption spectroscopy [65]. Combined X-ray and neutron diffraction experiments verified the ideal stoichiometry, but showed also sensitivity to intrinsic V-doping of the iron site, which suppresses superconductivity in Sr$_2$VO$_3$[Fe$_{0.91(1)}$V$_{0.09(1)}$]$_2$As$_2$ [66]. The role of the V atoms with respect to the electronic structure of Sr$_2$VO$_3$FeAs is still under discussion [67, 68]. Recent neutron [66] and photoemission [69] experiments point to highly correlated vanadium in the oxygen environment. The V-3$d$ orbitals are removed from the Fermi level by the magnetic exchange effects.

![Fig. 3](image-url) Fig. 3. The rhombohedral crystal structure of NdZnPO. The layers of edge-sharing ZnP$_{4/2}$ and ONd$_{4/2}$ tetrahedra are emphasized. For details see text.
the pnictide oxide chemistry. Na$_2$Ti$_2$(As,Sb)$_2$O

The still relatively low quality of the Sr$_2$VO$_3$FeAs samples.

splitting. However, the progress is somewhat hampered by

Further related compounds with stacked layers extend

the pnictide oxide chemistry. Na$_2$Ti$_2$(As,Sb)$_2$O [70] crystallizes with a modified anti-K$_2$NiF$_4$ type structure (I4/mmm) and exhibits anomalies in the magnetic susceptibility and resistivity [71]. BaTi$_2$As$_2$O contains analogue, but eclipsively stacked Ti$_2$OAs$_2$ layers [72]. A resistance anomaly around 200 K is suppressed by lithium doping in Ba$_{1-x}$Li$_x$Ti$_2$As$_2$O, but no superconductivity was found. (SrF)$_2$Ti$_2$Pn$_2$O ($Pn = \text{As, Sb}$) [73] is also derived from the Na$_2$Ti$_2$(As)$_2$O-type structure through replacing Na$^+$ by Sr$^{2+}$, and filling the tetrahedral voids with oxygen atoms as depicted in Fig. 4c. Anomalies appear at 200 K in the heat capacity and resistivity. A subtle structural transition was also detected, but without changes in the space group symmetry. Compounds with the A$_2$M$_5$Pn$_2$O$_7$ structure [74] have also been suggested as parent compounds for superconductors [75]. Sr$_3$Mn$_3$As$_2$O$_7$ contains alternating Mn$_2$As$_2$ and SrMnO$_2$ layers, where manganese atoms are tetrahedrally coordinated by phosphorus as well as in square planar oxygen coordination. Neutron diffraction experiments revealed G-type magnetic ordering in the Mn$_2$As$_2$ layer (3.50(4) $\mu_B$/Mn at 4 K) and non-magnetic manganese in the MnO$_2$ layer, which changes to an A-type ferrimagnetic structure in Sr$_3$Mn$_3$Cu$_2$As$_2$O$_7$. Herein, the Mn atoms in the Mn$_2$As$_2$ layers are ferromagnetically aligned (3.9(1) $\mu_B$/Mn), but antiferromagnetically between the layers [76, 77]. The structure of Nd$_2$Fe$_2$O$_5$Se$_2$ is similar [78], build up by Nd$_2$O$_5$ and Fe$_2$OSe$_2$ layers, where iron is six-fold coordinated by two oxygen and four selenium atoms. Antiferromagnetic ordering of the Fe spins occurs at 88 K with the moments oriented in the Fe–O bond direction [79]. An interesting large stacking variant represents La$_5$Cu$_4$As$_4$O$_4$Cl$_2$, which was obtained from a NaCl salt flux [80]. ThCr$_2$Si$_2$-like La[Cu$_2$As$_2$]$_2$ layers alternate with LaOCl blocks as shown in Fig. 4d.

Group-subgroup schemes – superstructures

Several of the iron pnictide and related structures (the parent structures of the superconducting phases) show small structural distortions due to the occurrence of a spin-density-wave, ordered vacancies, or ordered oxygen displacements. Systemization of such superstructures is most effective through group-subgroup schemes. In the present chapter we exemplarily present such schemes in the concise and compact Bärnighausen formalism [81–83].

At room temperature BaFe$_2$As$_2$ [42] adopts the tetragonal ThCr$_2$Si$_2$ type structure, space group I4/mmm. A structural phase transition occurs at 140 K [25]. The BaFe$_2$As$_2$ structure becomes orthorhombic, space group Fmmm, similar to the $\beta$-SrRh$_2$As$_2$-type [84]. This corresponds to a translationengleiche symmetry reduction of index 2. The tetragonal mesh (we list $a\sqrt{2}$ for better comparison, i.e. F4/mmm) of 560.38 $\times$ 560.38 pm distorts to 561.46 $\times$ 557.42 pm. In parallel, the c lattice parameter slightly contracts from the tetragonal (1301.68 pm) to the orthorhombic (1294.53 pm) phase [25]. The decoupling of the tetragonal a lattice parameter is the only gain of free parameters for this phase transition. As is evident from Fig. 5, we do not gain further free x, y, or z parameters, but lower site symmetries for all atoms. Thus, the phase transition leads to a slight flattening and distortion of the FeAs$_{4/4}$ tetrahedra (Fig. 6).

A structural distortion at low temperature has also been reported for BaNi$_2$As$_2$ [85]. These authors reported the low-temperature structure in the triclinic space group P1. This is astonishing, since LT-BaNi$_2$As$_2$ would have the lowest symmetry of all BaAl$_4$ superstructures; see the Bärnighausen tree in [86]. In most cases, the lowering of the symmetry proceeds via few, often only one step.
The nature of the BaFe$_2$As$_2$ structural phase transition is completely analogous to that in LaFeAsO \[41\] which contains similar layers of condensed FeAs$_{4/4}$ tetrahedra (vide infra). Starting from space group \(P\bar{4}/nmm\) we observe a \textit{translationengleiche} symmetry reduction (\(t_2\)) to space group \(Cmme\). The corresponding group-subgroup scheme is shown in Fig. 7. Again, the FeAs$_{4/4}$ tetrahedra are slightly flattened in LT-LaFeAsO with lower site symmetry.

The structure of La$_2$CdSe$_2$O$_2$ \[87, 88\] also derives from ZrCuSiAs type HT-LaFeAsO, however, with a distinct difference in the cadmium and selenium containing tetrahedral layer. The formal ionic formula splitting for this compound is $[\text{La}_2\text{O}_2]^{2+}\cdot[\text{CdSe}_2]^{2-}$. In order to charge-balance the insulating $[\text{La}_2\text{O}_2]^{2+}$ layers, only half of the transition metal positions need to be filled with divalent cadmium. The ordering pattern for the tetrahedral $[\text{CdSe}_2]^{2-}$ layers is shown in Fig. 8 and the corresponding group-subgroup scheme in Fig. 9. The symmetry reduction proceeds via a \textit{klassengleiche} transition of index 2 from \(P\bar{4}/nmm\) to \(P\bar{4}_2/\text{nmc}\), leading to superstructure reflections. Since every other cadmium atom is removed from the subcell layers in a checkered motif, we only observe corner-sharing CdSe$_{4/2}$ tetrahedra in the superstructure.

A further interesting example is the selenide oxide Ba$_2$ZnO$_2$Ag$_2$Se$_2$ \[89\], which crystallizes with a distortion variant of the Sr$_2$Cu$_2$CoO$_2$S$_2$ type structure \[90–92\]. This type is an intergrowth variant of $[\text{Ag}_2\text{Se}_2]$ tetrahedral layers (similar to LaFeAsO and BaFe$_2$As$_2$) and perovskite-related $[\text{Ba}_2\text{ZnO}_2]$ slabs. In the Sr$_2$Cu$_2$CoO$_2$S$_2$ type subcell structure, space group \(I\bar{4}/mmm\), the zinc atoms show an unusual ZnO$_2$ square plane (Fig. 10). However, in contrast to the Sr$_2$Cu$_2$CoO$_2$S$_2$ type compounds, if one places the ZnO$_2$ slab under tension (this is actually the case for the...
larger ions \( \text{Ba}^{2+} \), \( \text{Ag}^{+} \), and \( \text{Se}^{2-} \)), the square planar arrangement distorts and the structure forms discrete, linear \([\text{ZnO}_2]\) units.

The average structure in space group \( I4/mmm \) and the well ordered superstructure in space group \( Cmce \) are related by a group-subgroup scheme (Fig. 11). The corresponding symmetry reduction proceeds in two steps. First there is a \( \text{translationengleiche} \) transition from \( I4/mmm \) to \( Fmmm \), followed by a \( \text{klassengleiche} \) transition (\( k^2 \)) to \( Bbem \), a non-standard setting of \( Cmce \). The superstructure has twice the cell volume of the subcell. Besides the standardized data, we also list the transformation to the refined data in Fig. 11, in order to facilitate comparison with the published data.

The symmetry reduction has a drastic effect on the \( \text{Zn}--\text{O} \) distances. In the subcell the average \( \text{Zn}--\text{O} \) distances within the \( \text{ZnO}_2 \) squares are 214.2 pm. In the ordered superstructure always two oxygen atoms move towards the zinc atoms while the other two move away, leading to shorter (2/\( c^2 \)) 189.6 pm) and longer (2/\( c^2 \)) 238.9 pm) \( \text{Zn}--\text{O} \) distances. Thus, \( \text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2 \) is a rare example for the \( \text{Zn}^{2+} \text{d}^{10} \) ion in linear coordination. As is evident from the refined positional parameters, the maximum shifts from the subcell to the superstructure occur for the oxygen atoms, while the metal atoms almost remain at their original positions. The structural distortion is nicely underlined by bond valence sum (BVS) calculations, which show BVS = 1.35 for the subcell and 1.63 for the superstructure [89].

A last example concerns the structure of \( \text{Sr}_2\text{MnO}_2\text{Cu}_1.5\text{S}_2 \) [32, 93]. At room temperature this sulfide oxide is tetragonal, space group \( I4/mmm \) and shows a 75% random copper occupancy within the tetrahedral layer, similar to several \( \text{CeCu}_{1-x}\text{SO} \) samples [94, 95]. Upon cooling the sample below 240 K, long-range ordering of filled (75%) and vacant (25%) copper sites occurs (Fig. 12). The symmetry reduction proceeds via three steps (Fig. 13). The first two reductions, \( r^2 \) to \( Fmmm \) and

![Fig. 10.](image)

Fig. 10. The zinc (filled circles)-oxygen (open circles) substructures in the subcell and the superstructure of \( \text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2 \). The unit cells are marked by light grey shading. Relevant \( \text{Zn}--\text{O} \) distances are indicated. For details see text.

![Fig. 11.](image)

Fig. 11. Group-subgroup scheme in the Bümighausen formalism for the structures of \( \text{Sr}_2\text{Cu}_2\text{CoO}_2\text{S}_2 \) and \( \text{Ba}_2\text{ZnO}_2\text{Ag}_2\text{Se}_2 \). The indices for the \( \text{translationengleiche} \) and \( \text{klassengleiche} \) symmetry reductions and the evolution of the atomic parameters are given. In the last two columns the standardized and refined data are listed for better comparison with the published data. For details see text.

![Fig. 12.](image)

Fig. 12. The copper (filled circles)-sulfur (open circles) substructures in the subcell (75% occupancy of the copper site) and the superstructure of \( \text{Sr}_2\text{MnO}_2\text{Cu}_1\text{S}_2 \). The unit cells are marked by light grey shading. For details see text.
$k_2$ to $Bmem$, lead to an intermediate model, where still all (or half) of the copper sites would be filled. The third step ($k_2$) from $Bmem$ to $Ibam$ allows for a splitting of the $4a$ Cu site into two fourfold $Cu$ sites $4a$ and $4b$, of which the latter remains unoccupied in the ordered state. The vacancy formation has only tiny influence on the filled tetrahedral sites. One observes almost regular $CuS_4$ tetrahedra in the ordered low-temperature structure. The copper deficiency is driven by the manganese valence and an electron precise formulation $(2Sr_{2}^{+}+Mn_{2.5}^{+}+O_{2}\text{/Co}^{4-})_{4}$ is adequate. The manganese valence has been determined on the basis of XANES measurements [93].

**Structural flexibility**

Superconductivity in iron based pnictides was first discovered in the stoichiometric phosphate-oxide $LaOFeP$ [12], but the low $T_c$ of 4 K caused not much attention at that time. The breakthrough came in 2008 with the isotypic arsenide $La(O_{1-x}F_{x})FeAs$ [17]. Stoichiometric $LaOFeAs$ is non-superconducting, but a poor metal which exhibits a magneto-structural phase transition at 150 K [96]. Fluorine substitution increases the negative charge in the FeAs layers and is therefore called “electron doping”, which suppresses the phase transition and superconductivity emerges at 26 K. Replacing lanthanum by smaller rare earth ions increases the $T_c$ up to 55 K in $Sm(O_{0.85}F_{0.15})FeAs$ [18], which is the highest in iron based superconductors so far. Subsequently, the iron arsenides with $ZrCuSiAs$- and $ThCr_2Si_2$-type structures turned out to allow substitutions of all atom sites. Substitution of iron by small amounts of cobalt, e.g. in $Ba(Fe_{1-x}Co_x)_{2}As_2$ [97] or $La(O(Fe_{1-x}Co_x)_{2}As$ [98] induced superconductivity at 22 and 14 K, respectively. This kind of doping represents a remarkable difference to the cuprate compounds, where any, even small doping of the copper site is detrimental to superconductivity.

Also reducing the negative charge of the $(FeAs)_{d}/Co_{d}$ layer induces superconductivity in iron arsenides. Examples of such “hole doping” are the replacement of $La^{3+}$ by $Sr^{2+}$ in $(La_{1-x}Sr_{x})OFeAs$ ($T_c$ up to 25 K) [99] and substituting $Ba^{2+}$ by $K^+$ in $Ba_{1-y}K_{y}Fe_{2}As_{2}$ ($T_c$ up to 38 K) [23] or by $Na^+$ in $Ba_{1-y}Na_{y}Fe_{2}As_{2}$ ($T_c$ up to 34 K) [103]. Analogous substitutions of the alkaline earth by alkali ions in $SrFe_{2}As_{2}$ [101] and $CaFe_{2}As_{2}$ [102] have also been reported. Finally, it was found that even substitutions without changing the total electron count can induce superconductivity. This “isovalent doping” is possible by replacing iron with ruthenium in $Ba(Fe_{1-x}Ru_x)_{2}As_2$ [103] or arsenic with phosphorus in $BaFe_{2}(As_{1-x}P_x)_{2}$ [104] and $LaOFe(As_{1-x}P_x)$ [105]. Typically, much higher degrees of
substitution (30–40%) are required at isovalent substitution in comparison with electron- or hole-doping, where 5–20% are sufficient in most cases. Despite these diversified options of inducing superconductivity in parent compounds with FeAs layers, the resulting phase diagrams are remarkably similar and reminiscent to the cuprates. Superconductors with FeAs layers, the resulting phase diagrams are remarkably similar and reminiscent to the cuprates. Superconductivity emerges as the magneto-structural phase transition gets suppressed, and the superconducting domes generally involve a large composition range as shown for Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [24]. To what extend superconductivity and magnetic ordering co-exist in the underdoped region ($x \approx 0.15–0.25$ in Fig. 14) is still controversial. Findings from $^{57}$Fe-Mössbauer spectroscopy gave evidence of homogeneous co-existence, while $^{75}$As-NMR [106] and μSR [107] data indicated mesoscopic phase separation in magnetic and superconducting fractions. On the other hand, homogeneous co-existence is generally accepted in the Co-doped system Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [108] (see below).

While the effect of substitution on the electronic and magnetic properties has been intensively investigated with respect to the mechanism of superconductivity, not so much studies were published about the effects on the crystal structure. Potassium doping in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ leads to a significant linear elongation of the $c$-axis. The Fe–As bond lengths remain remarkably constant close to 240 pm, while the As–Fe–As angles become smaller and close to the ideal tetrahedral angle of 109.47° in Ba$_{0.8}$K$_{0.2}$Fe$_2$As$_2$ with the highest $T_c$ [24]. The structural changes are shown in Fig. 15. Interestingly, sodium substitution has an almost identical effect on the crystal structure, except for the unit cell volume, which is almost constant in the case of Ba$_{1-x}$Na$_x$Fe$_2$As$_2$, but decreases significantly by substitution with smaller Na$^+$ ions in Ba$_{1-x}$Na$_x$Fe$_2$As$_2$ [100]. It is quite remarkable that the critical temperature is not significantly changed by this rather large volume effect. The latter finding also challenges the report about the coincidence of the structural changes in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with those in undoped BaFe$_2$As$_2$ under pressure, where superconductivity emerges between 2.5 and 6 GPa [109]. A special role of the As–Fe–As angle has been presumed after Lee et al. [110] collected structural data of many pnictide superconductors and showed that the highest $T_c$'s occur if the tetrahedral angle is close to the ideal one. However, the true connection between the bond angle and superconducting pairing mechanism is not yet clear.

A notable argument for competing structural and superconducting order parameters in underdoped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ arose from a remarkable accurate structural study by Nandi et al. [108]. According to this, the orthorhombic distortion of the antiferromagnetic phase decreases below the onset temperature of superconductivity as shown in Fig. 16. However, the detailed crystal structure of the low-temperature phase is still unknown. Also the origin of the phase transition is not yet completely clear, in particular because the structural distortion occurs at temperatures well above the magnetic ordering in the 1111-compounds, while both appear simultaneously in the undoped 122-materials. Lv et al. suggested ordering of the iron $d_{x^2-y^2}$ orbitals [111], while nematic order of the magnetic moments was proposed by other authors [112].

Detailed studies of the effects of isovalent substitution on the structures of CeOFe(As$_{1-x}$P$_x$), Ba$_{1-x}$Sr$_x$Fe$_2$As$_2$ and BaFe$_2$(As$_{1-x}$P$_x$)$_2$ have been reported [113, 114]. In the latter case, it has been shown that arsenic and phosphorus are not exactly at the same coordinates in the unit cell, and that phosphorus doping is not a simple chemical pres-
sure effect, but a subtle reorganization of the crystal structure.

**Outlook**

Approximately 30 months have passed since the first paper of a La 1111 superconductor with \( T_C = 26 \) K was reported. More than 2000 papers have been already published to date. Although many iron-based superconductors have been found, each of them contains a square net of Fe\(^{2+}\) ions in tetrahedral coordination with pnictogen ions or chalcogenide ions. The electronic state near the Fermi level is almost governed by five Fe 3d orbitals and the contribution of the anion orbitals remains \( \sim 10\% \). We may thus regard these materials as iron-based superconductors. It has revealed that iron-based superconductors have several unique superconducting properties compared with high temperature cuprates and MgB\(_2\), i.e., high robustness to magnetic field, insensitiveness to magnetic impurities and small anisotropy of the physical properties. These features are favorable for applications in superconducting wires.

Perhaps, the most important but difficult subject in this area is to raise the \( T_C \) above 77 K. The maximum \( T_C \) attained to date is 56 K, which was obtained for the Sm 1111 compound reported in June, 2008. What is the primary factor controlling the \( T_C \) in these material systems? The crystal chemistry provided a clue to this issue. Lee et al. [110] examined a correlation between the \( T_C \) and the bond angle of \( Pn(Ch)-Fe-Pn(Ch) \), finding that the \( T_C \) is raised as the bond angle approaches to that (109.47\(^\circ\)) of the regular tetrahedron. Kuroki et al. [115] calculated the \( T_C \) on the assumption that these materials are spin-fluctuation mediated superconductors and proposed that the \( T_C \) is pushed up when the height (\( h_{pn} \)) of pnictogen(chalcogen) from the iron plane is increased. This idea was derived from a consideration of the topology change of the Fermi surface by the appearance/disappearance of a pocket reflecting the fact that the Fe \( d_{x^2-y^2} \) level is sensitive to \( h_{pn} \). Figures 17a and b summarize the data of \( T_C \) and the tetrahedral angle or \( h_{pn} \) for 5 types of parent compounds. Although both plots well explain the striking difference in \( T_C \) between LaFePO and LaFeAsO or among the REFeAsO (\( RE = \) La, Ce, Nd, and Sm) series, a reverse correlation was seen for the 122 systems or a part of the 11 systems. These two plots suggest the importance of the local structure around the iron. Ogino et al. [56] examined the effect of the thickness of the blocking layers between FeAs(P) layers on \( T_C \) in iron pnictides with perovskite-like layers, finding that the \( T_C \) is increased slightly but saturates around a thickness of \( \sim 1.5 \) nm. The tetrahedral angle around iron or the pnictogen height from the iron plane is only one structural parameter to predict the \( T_C \), although some exceptions are seen, at the present stage. The researchers are concentrating on finding materials with higher \( T_C \) following this tentative guide, expecting totally new high \( T_C \) materials which are far from this rule. Strike while the iron is hot. The authors believe this old saying is also true in the present case.

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