Arsenic chemistry of iron-based superconductors and strategy for novel superconducting materials

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ABSTRACT
The progress of materials discovery of iron-based superconductors is reviewed with the emphasis on the valence states and chemical bonds of arsenic. We demonstrate that monovalent As⁺ produces the 112-type CaFeAs₂ with arsenic zigzag chains. When co-doping of La and Sb is performed, the superconducting transition temperature rises to 47 K. In the 10-4-8-type Ca₁₀(Pt₄As₈)(Fe₂−ₓPtₓAs₂)₅, the divalent As²⁻ produces As₂ molecules, and creates an interlayer substance with PtAs₄ planar squares. The maximum superconducting transition temperature is 38 K. In the 122-type CaFe₂As₂, Rh doping induces a lattice collapse transition accompanying the formation of As₂ molecules between the adjacent FeAs layers. This transition can be viewed as a valence transition between As³⁻ and As²⁻. These properties of arsenic that produces various chemical bonds can be used to create new superconducting materials.

1. Introduction
Arsenic is a ‘pluripotent’ element. That is, arsenic, as seen with As⁰ (4p³), As⁻ (4p⁴), As²⁻ (4p⁵), and As³⁻ (4p⁶), takes various valence states (electron configurations).
For this reason, arsenic makes various chemical bonds and as a result, produces various crystal structures. In neutral arsenic $\text{As}^0 (4p^3)$, three electrons occupy each $p_x$, $p_y$, and $p_z$ atomic orbitals. The three unpaired electrons each form covalent bonds. An example of this is $\alpha$-As (space group $R\bar{3}m$, $D_{5d}^3$, #166). As shown in Figure 1(a), an arsenic atom makes chemical bonds with the adjacent three arsenic atoms. As a result, the crystal structure is distorted to become trigonal. In monovalent arsenic $\text{As}^-$ ($4p^4$), two unpaired electrons exist and two chemical bonds per As are made. Examples of this are the As zigzag chain and the As$_4$ tetramer. Zigzag chains appear in the 112-type iron-based superconductor $\text{Ca}_{1-x}\text{La}_x\text{FeAs}_2$ (space group $P2_1$, $C_{2v}^2$, #4), as shown in Figure 1(b) [1–5]. Tetramers appear in $\text{CoAs}_3$ and other Skutterudites [6]. Since $\text{As}^{2-}$ ($4p^5$) has a single unpaired electron, arsenic makes a single chemical bond. In other words, As forms an As$_2$ molecule. This can be seen in the $\text{BaCu}_2\text{As}_2$ shown in Figure 1(c), or in the collapsed tetragonal structure of the 122-type iron-based superconductor $\text{CaFe}_2\text{As}_2$ [7–14]. Furthermore, in $\text{As}^{3+}$ ($4p^6$) with an additional electron, the $4p$ orbital becomes a closed shell, and
arsenic does not form a covalent bond. As a result, arsenic becomes the isolated anion \( \text{As}^{3-} \). This structure can be seen in the \( \text{BaFe}_2\text{As}_2 \), shown in Figure 1(d) [15], or in the uncollapsed tetragonal structure of \( \text{CaFe}_2\text{As}_2 \) [7–14].

In this review paper, we introduce the recent progress of materials discovery of iron-based superconductors with the emphasis on the valence states and chemical bonds of arsenic. We focus on three materials: the 122-type \( \text{CaFe}_2\text{As}_2 \) in which the formation of \( \text{As–As} \) bonds between the adjacent \( \text{FeAs} \) layers results in the loss of magnetism and superconductivity [7–14]; the 10-4-8-type \( \text{Ca}_{10}(\text{Pt}_4\text{As}_8) \) \( (\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5 \), in which molecule-like \( \text{As}_2 \) exists in the \( \text{Pt}_4\text{As}_8 \) layers [16–19]; and the newly discovered 112-type \( \text{CaFeAs}_2 \) with infinite \( \text{As} \) zigzag chains [1–5]. \( \text{CaFeAs}_2 \) exhibits superconductivity as high as 47 K when \( \text{La} \) and \( \text{Sb} \) are co-doped [5].

2. Arsenic dimers in the 122-type structure

Figure 1(c) and (d) show the crystal structures of \( \text{BaCu}_2\text{As}_2 \) and \( \text{BaFe}_2\text{As}_2 \). Both compounds crystallize in the tetragonal \( \text{ThCr}_2\text{Si}_2 \)-type structure (space group \( I4/mmm, D_{4h}^{17} \) #139). However, the \( c \)-axis length is different sharply. This is because, while in \( \text{BaCu}_2\text{As}_2 \), \( \text{As–As} \) bonds, or in other words, \( \text{As}_2 \) molecules, are formed between the adjacent \( \text{CuAs} \) layers, in \( \text{BaFe}_2\text{As}_2 \), there is no covalent bond between \( \text{As} \) and \( \text{As} \) in the adjacent \( \text{FeAs} \) layers. The \( \text{As–As} \) distances in these two structures are, respectively, 2.558 and 3.390 Å. The respective chemical formulae are \( \text{Ba}^{2+}\text{Cu}^{+}\text{As}_2^{-} \) and \( \text{Ba}^{2+}\text{Fe}^{2+}\text{As}_3^{-} \). In \( \text{BaFe}_2\text{As}_2 \), since arsenic is trivalent and has a closed shell \( (4p^6) \), it does not make a covalent bond. On the other hand, in \( \text{BaCu}_2\text{As}_2 \), since arsenic is divalent, it makes a single covalent bond, or an \( \text{As}_2 \)
molecule. The $\text{As}_2$ molecular orbitals are, in order from the lowest energy, $\sigma$, $\pi$, $\pi^*$, and $\sigma^*$. In the neutral $\text{As}_2$ molecule, six electrons occupy the $\sigma$ and the twofold degenerate $\pi$ orbitals. When four more electrons are added, the $\pi^*$ orbital is completely occupied. As a result, the arsenic molecule is stable in a tetravalent state $\left(\text{As}_2\right)^{4-}$. When we focus on the $\text{As}_2$ molecule, the above chemical formula becomes $\text{Ba}^{2+}\text{Cu}^+\left(\text{As}_2\right)^{4-}$. The valence state of $\text{Cu}^+$ has been confirmed by photoemission measurements [20,21]. When two more electrons are supplied to the $\left(\text{As}_2\right)^{4-}$ molecule, the antibonding orbital $\sigma^*$ is occupied, and the molecule dissociates to become $\text{As}^{3-}$ [22,23].
According to Hoffmann [22,23], differences between the crystal structures of BaCu$_2$As$_2$ and BaFe$_2$As$_2$ can be understood by the relative relationship between the Fermi energy in the transition metal $d$ band and the energy of the As$_2$ antibonding orbital $\sigma^*$. In BaCu$_2$As$_2$, the Fermi energy of the Cu $3d$ band is lower than the energy of $\sigma^*$ orbital. As a result, the $\sigma^*$ orbital is unoccupied, and As$_2$ molecules are formed. In BaFe$_2$As$_2$, the Fermi energy of the Fe $3d$ band is higher than the energy of As$_2$ $\sigma^*$ orbital. As a result, since the antibonding $\sigma^*$ orbital is occupied, the As–As covalent bond is broken to become As$_3^{3−}$. This situation is schematically shown in Figure 2. The $3d$ orbital energy decreases as the atomic number, or equivalently positive nuclear charge, increases. On the other hand, the band filling increases with the increase in the atomic number. As a result, the Fermi energy $E_F$ decreases in the order of Fe, Co, Ni, and Cu.

Figure 3 shows the $c$-axis lengths of the BaTM$_2$As$_2$, SrTM$_2$As$_2$, and CaTM$_2$As$_2$ for the transition metal element TM. If the As–As bond is formed, the $c$-axis length becomes approximately 11 Å or less. For BaTM$_2$As$_2$, the As–As bond is formed between Ni and Cu. For Sr or Ca, which have smaller ionic radii than Ba, formation of the As–As bond occurs more easily: for SrTM$_2$As$_2$, the As–As bond is formed between Co and Ni, and for CaTM$_2$As$_2$, between Fe and Co. CaFe$_2$As$_2$ is a parent compound of iron-based superconductors. Therefore, in CaFe$_2$As$_2$, the interplay between superconductivity and the As$_2$ molecule formation can be investigated.

We used Rh in place of Co because tiny Rh doping can cause As$_2$ molecule formation to occur [9]. Figure 4 shows the $c$-axis parameter as a function of doping $x$ for Ca(Fe$_{1-x}$Rh$_x$)$_2$As$_2$ at 300 K. First, the $c$-parameter decreases gradually upon doping. At $x = 0.2$, the $c$-parameter length shrinks discontinuously.

**Figure 5.** Electronic phase diagram for Ca(Fe$_{1-x}$Rh$_x$)$_2$As$_2$ [9].
Note: AF and SC denote antiferromagnetic and superconducting phases, respectively.
by approximately 5%. This is due to $\text{As}_2$ molecule formation, and is a first-order structural phase transition. The crystal structure symmetry remains unchanged across the transition as the tetragonal $\text{ThCr}_2\text{Si}_2$-type (space group $I\overline{4}mnm$). Since the volume decreases discontinuously, this transition is called as lattice collapse transition. The phase where the $\text{As}_2$ molecule is broken is called the uncollapsed phase, and the phase where the $\text{As}_2$ molecule is formed is called the collapsed phase. Interestingly, even if it is an uncollapsed phase at room temperature, thermal contraction promotes the formation of $\text{As}_2$ molecule and the phase transition to a collapsed phase occurs at low temperatures. Figure 5 shows a temperature–composition phase diagram for $\text{Ca(Fe}_{1-x}\text{Rh}_{x})_2\text{As}_2$. For example, the lattice collapse transition temperature is approximately 50 K at $x = 0.024$. At such a low temperature, and moreover in a solid state, it is surprising that $\text{As}_2$ molecule formation, or 'chemical reaction,' takes place.

It should be noted here that the electron count of $\text{Ba}^{2+}\text{Cu}_2^+\left(\text{As}_2\right)^{4-}$ is reasonable because the Cu $3d$ orbitals are well below the Fermi level and fully occupied ($3d^{10}$) [20]. In contrast, a simple electron count, such as $\text{Ca}^{2+}\text{Fe}_2^+\left(\text{As}_2\right)^{4-}$, cannot be applied because of the significant hybridization between Fe $3d$ and As $4p$ orbitals exists in the collapsed phase of $\text{CaFe}_2\text{As}_2$ [24]. However, a fractional electron count $\text{Ca}^{2+}\text{Fe}_{2-\delta}^+\left(\text{As}_2\right)^{4+2\delta}$ is likely, where $0 < \delta < 1$ denotes the number of electrons transferred from As $4p$ to Fe $3d$ orbitals. The reduction of negative valence of As is consistent with the observed shift of the As core level in the collapsed phase of $\text{Ca(Fe}_{1-x}\text{Rh}_{x})_2\text{As}_2$ [25].

Superconductivity appears in the uncollapsed tetragonal phase following the suppression of the antiferromagnetic ordering upon Rh doping [9]. The superconducting phase is limited to a narrow composition in the $x = 0.02$ region. In the uncollapsed phase, antiferromagnetic fluctuations are present, as observed by inelastic neutron and NMR/NQR measurements [11–14], and the electrical resistivity exhibits $T^{1.5}$ behavior [9,10], which is likely due to magnetic fluctuations. In the collapsed phase, antiferromagnetic fluctuations disappear [11–14], and the electrical resistivity shows a temperature dependence of $T^2$ [9,10], a hallmark of Fermi liquid. In this way, $\text{As}_2$ molecule formation causes the iron magnetic moment to disappear, and the superconducting phase disappears [7–14]. The $\text{As}_2$ molecule formation also causes increased interlayer interactions, which result in the loss of the Fermi surface nesting [25,26]. Both should be relevant to the disappearance of superconducting phase.

The lattice collapse transition of $\text{CaFe}_2\text{As}_2$ can be viewed as an arsenic valence transition. This is because the As valence in the uncollapsed phase is $\text{As}^{3-}$, and in the collapsed phase, is $\text{As}^{2-}$. As mentioned above, this phase transition is a first-order, accompanying a discontinuous decrease in the lattice volume, and the crystal structure symmetry remains unchanged. At the same time, the iron magnetic moment disappears. This is similar to the cerium $\alpha$$\rightarrow$$\gamma$ phase transition [27]. Cerium valence in the high-temperature phase $\gamma$-Ce is trivalent ($\text{Ce}^{3+}$, $4f^1$), and in the low-temperature phase $\alpha$-Ce, is tetravalent ($\text{Ce}^{4+}$, $4f^0$). The $\alpha$$\rightarrow$$\gamma$
transition is a first-order, and the crystal structure symmetry remains unchanged as face-centered cubic (space group $Fm\bar{3}m$, $O_{h}^{5}$, #225). With this transition, the volume decreases by approximately 15%, and the Ce magnetic moment disappears in the low-temperature phase. This first-order phase transition line terminates at a critical point of approximately 600 K and 2 GPa [27]. In the heavy-fermion superconductor CeCu$_2$Si$_2$, the temperature of the critical point of the Ce valence transition is reduced to near absolute zero, at which 'high-temperature' superconductivity emerges [28–30]. When hydrostatic pressure and Ge doping are applied to CeCu$_2$Si$_2$, the antiferromagnetic phase is suppressed and a superconducting phase with a maximum $T_c = 0.4$ K appears. By further applying pressure, the second superconducting phase with a maximum $T_c = 1$ K appears at the vicinity of the quantum critical point of Ce valence transition. The latter is considered to be superconductivity mediated by valence fluctuations, while the former by spin fluctuations, suggesting valence fluctuations are favorable for enhancing superconductivity. The lattice collapse transition of CaFe$_2$As$_2$, like the $\alpha$–$\gamma$ transition of Ce, is also expected to have a critical point at high temperatures. If this critical point could be lowered all the way to absolute zero, there is a possibility that superconductivity mediated by the As valence quantum fluctuations would emerge. In CaFe$_2$As$_2$ doped with La and P, a superconducting phase with $T_c = 45$ K has been discovered in a region distant from the antiferromagnetic phase [31]. This observation raises interest in the As valence transition of iron-based superconductors.

### 3. Arsenic dimers in the 10-4-8-type structure

When we performed doping various transition metal elements into CaFe$_2$As$_2$, we noticed that weak superconductivity appeared at high temperatures exceeding 30 K, limited to the case of Pt doping. As a result of trial-and-error, we confirmed that this superconductor was Ca$_{10}$$(Pt_{4}As_{8})(Fe_{2-x}Pt_{x}As_{2})_5$, currently called the 10-4-8-type [16]. The maximum observed value of the superconducting transition temperature was 38 K. In addition, the 10-3-8-type Ca$_{10}$$(Pt_{3}As_{8})(Fe_{2-x}Pt_{x}As_{2})_5$...
with lower $T_c$ values was confirmed [16]. Ni et al. [17] and Löhnert et al. [18] also discovered same compounds in the same time period.

Figure 6 shows the crystal structure of $\text{Ca}_{10}(\text{Pt}_4\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$. Between the superconducting FeAs layers, a Pt$_4$As$_8$ layer exists. This layer is formed from corner sharing PtAs$_4$ planar squares. These PtAs$_4$ planar squares are alternately rotated, and As$_2$ molecules are formed between the adjacent squares. The 10-3-8-type $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_{2-x}\text{Pt}_x\text{As}_2)_5$ in which Pt is periodically vacant also exists [16–19]. This is the parent compound for this group, since it can be expressed as $\text{Ca}^{2+}_{2} \text{Pt}^{2+}_{3} (\text{As}_2)^{4-} (\text{Fe}^{2+}_{2} \text{As}^{3-}_2)^{5-}$ for $x = 0$.

This compound is also important from the perspective of coordination chemistry. Fe$^{2+}$ favors tetrahedral or octahedral coordination. In fact, in iron-based superconductors, edge-sharing FeAs$_4$ tetrahedra form superconducting FeAs layers. On the other hand, Pt$^{2+}$ favors planar square coordination [32]. Planar square coordination also appears in complexes that include Ni$^{2+}$ or Pd$^{2+}$, and is the characteristic of the $d^8$ configuration [32]. In fact, reflecting the favoring by Fe$^{2+}$ and Pt$^{2+}$ of differing coordination, the platinum solubility limit in $\text{Ca}(\text{Fe}_{1-x}\text{Pt}_x)\text{As}_2$ was low, at $x = 0.08$ [33]. This shows that the substitution of Pt for Fe at the tetrahedral site is difficult. Cobalt and other transition metal elements that favor tetrahedral coordination exhibit continuous solid solution with Fe. Therefore, when the Fe favoring tetrahedral coordination is mixed with Pt favoring planar square coordination, it appears that, because they do not favor formation of a solid solution in nature, a new compound, 10-4-8-type, is produced. In the same way, compounds including the PdAs$_4$ planar squares [34–36] and IrAs$_4$ planar squares [37–40] were discovered. Since Ir$^{2+}$ favors tetrahedral coordination rather than planar square coordination, the crystal structure is unstable, and shows a structural phase transition at low temperatures [38,39].

**Figure 7.** Crystal structures of (a) CaFeAsF [42,43] and, (b) Ca$_{1-x}$La$_x$FeAs$_2$ [1].
4. Arsenic chains in the 112-type structure

Finally, we introduce an iron-based superconductor that is created using monovalent As\textsuperscript{−}. LaFeAsO is a compound that serves as a prototype for iron-based superconductors [41]. The crystal structure is a laminated structure, alternating between fluorite and antifluorite-type layers of LaO and FeAs, respectively. In the fluorite-type structure, anions are found at the tetrahedral coordination center, while in the antifluorite-type structure, cations are found at the center. The replacement of LaO layers to CaF layers results in CaFeAsF [42,43]. With awareness of valence, this becomes Ca\textsuperscript{2+}Fe\textsuperscript{2+}As\textsuperscript{3−}F\textsuperscript{−}. If the hydride H\textsuperscript{−} is substituted for the fluoride ion F\textsuperscript{−}, then Ca\textsuperscript{2+}Fe\textsuperscript{2+}As\textsuperscript{3−}H\textsuperscript{−} results [44]. Both CaFeAsF and CaFeAsH exhibit superconductivity when doped [42–44]. For a monovalent anion, there is also the halogen Cl\textsuperscript{−}, Br\textsuperscript{−}, or I\textsuperscript{−}. However, an 1111-type structure containing these elements does not exist. Since the ion radius is large, it appears that the fluorite structure is not formed. So then, is this the end for compounds that are derived from the 1111-type structure? Here, let us introduce the newly discovered 112-type CaFeAs\textsubscript{2} [1–5]. As was mentioned at the outset, arsenic can take the monovalent state As\textsuperscript{−}. This As\textsuperscript{−} can be substituted for F\textsuperscript{−} or H\textsuperscript{−}. In this manner, Ca\textsuperscript{2+}Fe\textsuperscript{2+}As\textsuperscript{3−}As\textsuperscript{−} = CaFeAs\textsubscript{2} is obtained [41]. Synthesizing this compound requires approximately 10% La doping [1]. Without La, the 122-type CaFe\textsubscript{2}As\textsubscript{2} is yielded. Figure 7 shows the crystal structure of Ca\textsubscript{1−x}La\textsubscript{x}FeAs\textsubscript{2}, in which arsenic zigzag chain structure that is characteristic of As\textsuperscript{−} can be seen. Because of the weak ionic character of As\textsuperscript{−}, the distance between Ca and As widens. In contrast, the distance between Ca and F(H) is considerably short due to the strong ionic character of F\textsuperscript{−} and H\textsuperscript{−}. This compound exhibits superconductivity at 35 K [1,4,5]. Furthermore, in the Ca\textsubscript{1−x}La\textsubscript{x}Fe(As\textsubscript{1−y}Sb\textsubscript{y})\textsubscript{2} simultaneously doped with La and Sb, the superconducting transition temperature rises up to 47 K [5]. According to single crystal X-ray structure analysis, Sb substitutes preferably to As in zigzag chains, rather than As in the FeAs layer [45], as predicted by first-principles calculations [46]. In contrast, excess doping of La causes antiferromagnetic and structural phase transitions [47–49], which results in loss of superconductivity. The observation of optical second-harmonic generation confirmed the lack of spatial inversion symmetry for Ca\textsubscript{1−x}La\textsubscript{x}FeAs\textsubscript{2} [49], which makes the 112-type a unique among iron-based superconductors.

5. Conclusion

In this review paper, we introduced the progress of novel iron-based superconducting materials utilizing the ‘pluripotency’ of arsenic, such as the arsenic electron count of various valence states to create various chemical bonds and various crystal structures. We have demonstrated that monovalent As\textsuperscript{−} plays an important role to produce the 112-type CaFeAs\textsubscript{2} with arsenic zigzag chains. When co-doping
of La and Sb was performed, the superconducting transition temperature rose to 47 K. In the 10-4-8-type Ca$_{10}$(Pt$_4$As$_8$)(Fe$_{2-x}$Pt$_x$As$_2$)$_5$, the divalent As$^{2-}$ produced an As$_2$ molecule, and created an interlayer substance from PtAs$_4$ planar squares. The maximum superconducting transition temperature was 38 K. In the 122-type CaFe$_2$As$_2$, Rh doping caused a lattice collapse transition accompanying the formation of an As$_2$ molecule between the FeAs layers.

The results shown in this review paper provide two hints regarding the strategy for new superconductors. The first is that, when two energies compete, interesting phenomena will occur. In the iron-based superconductors, the Fe $3d$ orbital and the As $4p$ orbital energies competed. Owing to this competition, a ‘chemical reaction’ in formation of the As$_2$ molecules occurred at the low temperature of 50 K. This transition could be viewed as a valence transition between the trivalent As$^{3-}$ and divalent As$^{2-}$. By analogy with heavy fermion superconductors, arsenic valence transition may be used for further enhancing superconductivity if a quantum critical point was realized. The other was that when setting a problematic situation, nature presents interesting answers. In this research, as a result of mixing elements such as Fe and Pt that favor differing coordination environments (tetrahedral and planar square coordination), a new interlayer substance called Pt$_4$As$_8$ was precipitated, and a new iron-based superconductor called 10-4-8-type was created.

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