

Chemistry in Superconductors

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Abstract

Superconductors with exotic physical properties are critical to current and future technology. In this review, we highlight several important superconducting families and focus on their crystal structure, chemical bonding, and superconductivity correlations. We connect superconducting materials with chemical bonding interactions based on their structure-property relationships, elucidating our empirically chemical approaches and other methods used in the discovery of new superconductors. Furthermore, we provide some technical strategies to synthesize superconductors and basic but important characterization for chemists needed when reporting new superconductors. In the end, we share our thoughts on how to make new superconductors and where chemists can work on in the superconductivity field. This review is written using chemical terms, with a focus on providing some chemically intuitive thoughts on superconducting materials design.

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1. Brief Introduction to the History of Superconductivity and Applications

Superconductors provide magnetic flux field expulsion and zero-resistance when electricity flows through them.¹ Moreover, superconducting materials have broad applications in many fields, such as grids that can transmit power without energy loss, ultra-fast levitating trains that ride frictionless magnets instead of rails, and quantum computing devices that use superposition and quantum entanglement to perform computation.²⁻⁷ As the most effective energy carrier, electricity is clean, versatile, and pervasive. However, power losses are produced when the electrical current flows in the coils and the magnetic field alternates in the core. For example, electric transformer losses in the current grid are substantial. Using eco-friendly superconducting materials to replace the current grid can enormously improve the efficiency of electric transmission. In modern technology, superconducting Al, Nb and Ta are widely used in superconducting qubits for quantum computers for its preservation of quantum coherence.⁸ However, the application of superconductors is far from real due to their low superconducting transition temperatures. Thus, pursuing materials that are superconducting under ambient condition, i.e., room temperature and ambient pressure, is one of the major goals for physicists, chemists and materials scientists.

Superconductivity was firstly discovered by Onnes in Hg with a critical temperature (T_c) of 4.2 K in 1911.⁹ Ever since its discovery, it has stimulated significant interest in the research community to look for new superconductors with a higher transition temperature (T_c), new phenomena closely coupled with superconductivity, and new theories to understand the superconducting mechanism. Subsequently, researchers discovered many superconducting families of materials in different elements, alloys, intermetallic compounds and oxides in various forms, either bulk or thin film.^{2,10} Figure 1 shows the timeline of several major groups of superconductors and highlights the most representative ones in them. Here in the first section, we

will briefly introduce some representative types of superconductors in the order of time. Note that this review is not an exhaustive introduction to superconductors, so we will only discuss several representative ones that are superconducting at the highest temperatures or discovered earliest.

In the 1950s, the Bardeen-Cooper-Schrieffer theory (BCS)¹¹ successfully explained the mechanism of phonon-mediated superconductivity. This well-known superconductivity mechanism was established by John Bardeen, Leon Cooper, and John Robert Schrieffer. The fundamental picture of the BCS theory is that electron-phonon coupling induces a superconducting state by pairing up electrons with opposite spins and crystal momenta (that is, total momentum zero). The Cooper pair, as part of a highly correlated state, is free to move through the lattice, in contrast to a localized electron pair. Moreover, in BCS theory, the pairing of electrons occurs in momentum space, a space defined reciprocally to real space, and the Cooper pair cannot be described locally. The BCS theory fails to provide definite theoretical predications for new superconductors, therefore, the synthesis of novel superconductors is still plagued by mystery and challenges. In addition, the superconductors whose superconducting mechanisms can be explained by BCS theory are normally called BCS superconductors (SCs) or conventional SCs (CSCs) while others are called unconventional SCs (UCSCs).

From a chemical viewpoint, the BCS theory can be simplified, but may not be rigorous enough, into the following picture: when the material is in the superconducting state, two moving electrons with opposite wave vectors and spins in a lattice attract each other and form Cooper pair through phonon mediation where the phonon is the vibration of lattice. Cooper pairs move in the lattice as a condensate without resistance. In order to break one Cooper pair, it requires the energy of 2Δ , in which Δ is the superconducting energy gap.¹¹ This indicates that the energy from the oscillation of atoms is too weak to break Cooper pairs and thus zero resistance can persist. The

relation between Δ and T_c is given by this equation: $2 \Delta (0) = 3.52 k_B T_c$, where k_B is the Boltzmann constant and $\Delta (0)$ indicates the theoretical superconducting energy gap at 0 K.

BCS theory and its modifications can help to predict the superconducting critical temperature by the following formula: $T_c = 1.14 \frac{\hbar \omega_D}{2\pi k_B} e^{-1/N(E_F)\lambda}$, where $\hbar$ is Planck's constant, ω_D is the Debye frequency, k_B is the Boltzmann constant, $N(E_F)$ is the density of states (DOS) at the Fermi level (E_F) and λ is the electron-phonon interaction parameter.^{12,13} A larger density of states (DOS) at the Fermi level $N(E_F)$ or electron-phonon interactions or both lead to a higher T_c superconductor. However, the structural stability of a compound would be under a high risk if the electronic structure has a large DOS at the Fermi level.¹⁴ Therefore, superconductivity can be considered as a competing balance between stable geometric structures and unstable electronic structures. Several models included Allen & Dynes and Eliashberg equations are used to combine the experimental results and theoretical superconducting transition temperatures.^{15,16} Among them, McMillan modified the equation is widely used by experimental scientists to obtain the theoretical T_c for strong coupled superconductors¹⁷:

$$T_c = \frac{\omega_D}{1.45} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]$$

where λ is the electron-phonon coupling parameter, μ^* is the Coulomb coupling constant, and ω_D is the Debye temperature. McMillan also predicted the upper limit of T_c for some classic superconductors, such as Nb, Pb, Nb₃Sn and V₃Si to be 22, 9.2, 28 and 40 K.¹⁸ This upper critical temperature limit of 40 K was usually regarded as the upper limit of T_c for all BCS-type superconductors although McMillan himself did never claim that.¹⁸ The “ T_c ” of 40 K was then exceeded by pressure-induced superconductivity but found to be correct for all electron-phonon coupling induced superconductors under ambient pressure until now.

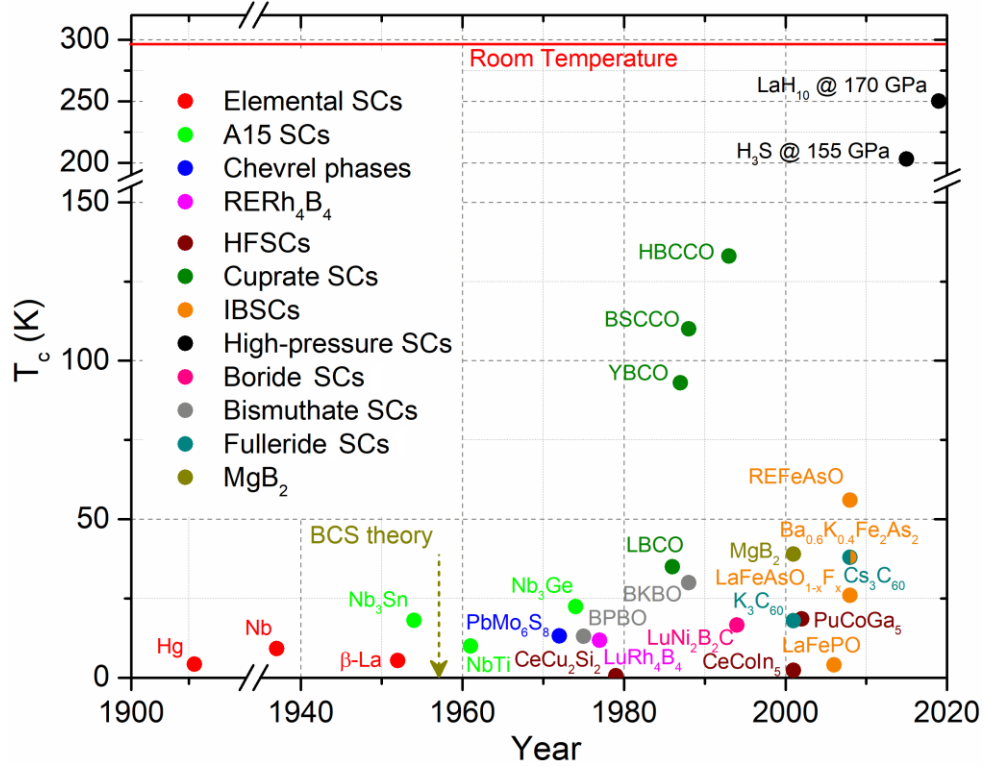


Figure 1. Timeline of several superconductor discoveries marked as before and after BCS theory. SCs: superconductors. A15 SCs: superconductors deriving from Cr_3Si structure type. Chevrel phases: MMo_6S_8 where $M = \text{Pb}$ and rare-earth (RE). RERh_4B_4 : RE represents rare-earth elements. HFSCs: heavy-Fermion superconductors. LBCO: Ba-doped La_2CuO_4 (LBCO). YBCO: $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. BSCCO: $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ where n is positive integer. HBCCO: $\text{Hg}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+m+2}$ where $m = 1$ and $n = 1$ to 7. IBSCs: iron-based superconductors.

One of the largest families of superconductors before the high- T_c superconductor era is the cubic A15 structure, which was well studied for their high T_c s and high upper critical fields (H_{c2} s). More specific review articles about A15 superconductors can be found from Refs. 19-22.¹⁹⁻²² The A15 structure was first discovered as an allotrope of tungsten, thus it can also be named as the β -W structure while A15 is a Strukturbericht designation indicating the structure is formed by the same element.^{23,24} Since it was originated from β -W structure, the derived structures were called A15 structure type. The superconducting A15 compounds are deriving from non-superconducting Cr_3Si , i.e., A_3B -type compounds. When it turns to superconductors, A is usually transition metals, such as Nb, V and Mo while B site is occupied by group IIIA to IVA elements, for example, Sn,

Ga and Ge. The superconducting mechanism of A15 superconductors is regarded as phonon-mediated, thus conventional (CSCs).²⁵

Before the discovery of Chevrel phases, which is a series of new phases, MMo_6S_8 where $\text{M} = \text{Cu, Zn, Mg, Ag, Cd, Sn, Pb}$ and rare-earth (RE), magnetic ordering was supposed to be incompatible with superconductivity according to BCS theory because the magnetic field or moment can interact with Cooper pairs and, thus, destroy superconductivity by raising the energy of one of the electrons in the Cooper pair.²⁶ However, Matthias et al. found superconducting signal in all reported phases except for ones containing RE.²⁷ More review articles about Chevrel superconductors can be found from Refs. 28-30.^{28,29,30} Superconducting critical temperature was found to be 13.2 K when $\text{M} = \text{Pb}$ as the highest in this series.³⁰ The superconductivity in REMo_6S_8 was then emerging in 1975 and the Se-version of Chevrel phase, REMo_6Se_8 ($\text{RE} = \text{lanthanide elements except Pm}$) and YMo_6Se_8 , was reported to host superconductivity in 1976. The highest T_c was obtained in LaMo_6Se_8 to be 11.39 K.³¹ Also, in 1977, Matthias et al. discovered another new family of rare-earth-contained superconductors, RERh_4B_4 ($\text{RE} = \text{Y, Nd, Sm, Er, Tm, Lu, and Th}$) where magnetism was found to be interacting with superconductivity.³² Whether the superconducting mechanism of Chevrel phases and RERh_4B_4 is unconventional is still under debate, however, in the late 1970s, another novel rare-earth-based superconductor, CeCu_2Si_2 surprised the community by its distinct superconductivity mechanism and was regarded as UCSC.³³ The group of related materials was named heavy-Fermion superconductors (HFSCs).³⁴ More discussion of HFSCs can be found in section 2.3. A detailed review of unconventional superconductivity of HFSCs can be found from Ref. 35.³⁵

Oxides were not seriously considered by researchers due to their localized electrons which normally lead to large bandgaps. Only several non-cuprate oxide superconductors were discovered

with T_c above 10 K before 1986. This includes spinel phase LiTi_2O_4 by Johnston et al. in 1973 with T_c at ~ 14 K.³⁶ Bismuthate $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ by Sleight et al. in 1975 with T_c at 13 K³⁷ (the T_c was pushed higher, to 30 K in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ by Cava et al. in 1988)³⁸. In 1986, superconductivity with $T_c = 30$ K was found in the Ba-doped antiferromagnetic insulator La_2CuO_4 , which inaugurated the era of high T_c cuprate superconductors.³⁹ More than 200 cuprate superconductors were discovered afterward and stimulated worldwide intensive research interest to understand the exotic superconductivity in this large family of compounds. This includes $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ^{40,41,42} the first superconductor with T_c above the liquid nitrogen boiling temperature, $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$,⁴³⁻⁴⁷ $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$, and $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3-\delta}$ where $n = 1, 2, 3, \dots$. The highest T_c in this family is 135 K at ambient pressure and 164 K under high pressure, obtained in 1994.⁴⁸⁻⁶⁵ Most of these compounds contain functional CuO_2 layers that exhibit specific interlayer distances while superconducting mechanism differs from what was demonstrated in BCS theory, thus UCSCs. Details can be found in section 2.4. A comprehensive review of hole-doped cuprate superconductors can be found from Refs. 66-67.^{66,67}

The interest in looking for superconductivity in hydrocarbons and organic compounds dates back to the 1950s, when it was suggested by London⁶⁸, and was further examined theoretically by Little⁶⁹ in 1964. The first organic superconductor was achieved in $(\text{TMTSF})_2\text{PF}_6$ (TMTSF = tetramethyltetraselenafulvalene) with $T_c = 0.9$ K at an external pressure of 1.1 GPa by Jérôme et al. in 1979⁷⁰ and extended to a few more Fabre and Bechgaard salt compounds.⁷¹⁻⁷⁴ On the other hand, pioneered by Dresselhaus et al.,⁷⁵ extensive studies were also carried out in graphite intercalation compounds, with different intercalation stages, with highest T_c 's of 11.5 & 6.5 K for CaC_6 and YbC_6 , respectively.⁷⁶ Following the discovery of Buckyball-structure C_{60} in 1985,⁷⁷ attempts concentrating on tuning C_{60} into superconductors grew explosively, resulting in many

reports in 1991 on superconducting fullerenes A_3C_{60} ($A=K, Rb, Cs$) with a face-centered cubic (*f.c.c.*) structure.^{78–81} The highest T_c of 38 K was found for *fcc* Cs_3C_{60} in 2008.⁸² In 2001, a high T_c , 39 K, was discovered in the well-known compound MgB_2 with a honeycomb B lattice and multiple-band superconductivity. Discovered by Akimitsu et al, this opened a new direction of searching for new superconductors in systems containing the light elements B and C, yet the T_c of MgB_2 remains highest and it still holds the highest T_c among all CSCs.⁸³

In 2008, the discovery of Fe-based superconductors generated another breakthrough in the unconventional superconductor family.⁸⁴ This breakthrough can be traced back to the discovery of novel transparent conductors in layered LaTPO ($T = Fe$ and Ni) compounds by Hosono's group after 2006.^{85,86} These compounds were first synthesized by Zimmer, et al. in 1995⁸⁷ and Quebe et al. in 2000.⁸⁸ However, no doping trial tests or physical property measurements on these compounds were performed by the beginning of the pnictide superconductor era. Hosono's group first reported superconductivity at 5 K in $LaFePO$ in 2006.⁸⁵ In 2008, layered $LaFeAsO_{0.9}F_{0.1}$ was reported to be superconducting around 26 K at ambient pressure⁸⁴ and later at 43 K under applied pressures up to 4 GPa.⁸⁹ The transition temperature T_c soon rose to 56 K at ambient pressure.⁹⁰ By revealing the concept of constructing new superconductors with the effective FeAs layers and tuning the valence electron concentration in the layers, several families of high- T_c Fe-based superconductors have been discovered, which includes the 1111 phase ($RFeAsO$, where R = rare earth),^{84,85,89–92} the 122 phase ($AeFe_2As_2$, AFe_2As_2 , and $A_{1-x}Fe_{2-y}Se_2$, where Ae = alkaline earth Ca, Sr, Ba , and A = alkaline metals Na, K, Rb, Cs)^{93,94–106} the 111 phase ($AFeAs$, where A = alkaline metal Li, Na)^{107–109} and the 11 phase ($FeSe$)^{110,111}. These Fe-based superconductors crystalize in structures that contain layers of edge-sharing $FeAs_4$ or $FeSe_4$ tetrahedra as charge carrier layers. Incorporating different charge reservoir layers between the charge carrier FeAs layers led to the

discovery of several new phases including $(\text{Sr}_3\text{Sc}_2\text{O}_5)\text{Fe}_2\text{As}_2$ ¹¹², $(\text{Sr}_2\text{VO}_3)_2\text{Fe}_2\text{As}_2$ ¹¹³, $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$ ¹¹⁴ and the so-called 10-3-8 $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$ and 10-4-8 $\text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5$ superconductors¹¹⁵. The 10-3-8 and 10-4-8 phases have novel crystal structures with the same -Ca-Pt_nAs₈-FeAs-Ca- stacking. The major difference in their structures lies in the Pt_nAs₈ layers, which are viewed as a skutterudite structure, a common crystal structure type in binary pnictides. These two structurally and chemically similar compounds with non-trivial Pt_nAs₈ layers inspire the further search for new high T_c superconductors by assembling multiple building blocks such as FeAs and Pt_nAs₈. A detailed review of IBSCs can be found from Ref.116.¹¹⁶

Superconducting materials are widely used in many applications, such as electrical grids that can transmit power without energy loss, ultra-fast levitating trains that ride frictionless magnets instead of rails, and quantum computing devices that use superposition and quantum entanglement to perform computation.^{117–120} For example, superconductors are critical components in magnetic resonance imaging (MRI) and experimental superconducting magnets which generate a large magnetic field. Currently, NbTi and Nb₃Sn are commercially available superconducting wires. NbTi is used for the superconducting magnets with low and intermediate magnetic fields, whereas Nb₃Sn wires can meet the requirements for high magnetic fields. Electricity, as the most effective energy carrier, is clean, versatile, and pervasive. Meanwhile, power losses are produced when the electrical current flows in the coils and the magnetic field alternates in the core. Using eco-friendly superconducting materials to replace the current grid can enormously improve the efficiency of electric transmission. Among various high-T_c superconductors, Yttrium-based superconducting wire (YBCO)¹²¹ has a higher critical current in magnetic fields than other superconductors and a higher critical temperature, above liquid nitrogen

temperature, which can provide high-performance superconducting applications at broader ranges in both magnetic field and temperature regions. Superconducting Josephson junction devices have been used in superconducting quantum interference device (SQUID) magnetometers to measure extremely small magnetic fields, and in ultrasensitive sensors.¹²² Moreover, superconductors are key to superconducting quantum computing, which is an implementation of a quantum computer in superconducting electronic circuits.^{117–120} The superconducting electronic circuit is a Josephson junction device, which consists of two or more superconductors (Nb) coupled by an insulator (Al_2O_3). Very recently, deLeon and co-workers replaced superconducting Nb with superconducting Ta in superconducting transmon qubits, with coherence times exceeding 0.3 milliseconds, realized in 2020.⁸

In this work, we will review structural perspectives in superconductors and the relationships among representative superconductors, how to use empirical rules in chemistry to discover new superconductors, several simple yet important characterization methods when claiming to find new superconductors, and some future directions in superconductivity. Given the long history and broad interest of superconductivity, it will not be possible at all to include all the important aspects and references that exist in this important field.

2. Structural Relationships among Representative Superconductors

Based on the discovered superconductors, superconductivity was normally found within a typical structural family, i.e., by discovering superconductivity in one compound in a structural family, one can easily perform chemical modification by substituting the elements to the ones in the same/near groups to achieve new superconducting phases, typically with the same structure type while sometimes led to the distorted ones. Therefore, in section 2 we will classify some well-known superconductors by their structure types and try to find out the structural features that can help us with future research on novel superconductors.

2.1. A15 Superconductors and their Derivates.

The superconducting A15 compounds, for instance, Nb_3Sn , are derived from non-superconducting Cr_3Si , i.e., A_3B -type compounds, crystallizing in space group $P m-3n$.²³ The crystal structure of Nb_3Sn , one representative of A15 superconductors, is shown in Figure 2(a). B atoms occupy the corner and body centers of the cubic structure while the A atoms form linear chains along the orthogonal cubic crystal axes x , y and z . Moreover, two body-center-position B atoms and two corner-position B atoms construct an $\text{A}@\text{B}_4$ tetrahedron with one A atom. Looking from the C_3 axis of the unit cell, two groups of $\text{A}@\text{B}_4$ tetrahedra can be found stacking in a staggered manner, which, in terms of chemical structural stability, is favored by the total energy of the structure. Moreover, as shown in Figure 2(b), based on the fragment formalism for making superconductors, we find that the superconducting family $\text{A}_3\text{T}_4\text{Sn}_{13}$ (A= alkali-earth; T= Co, Rh, Ir)^{123,124} can be considered as putting edge-shared RhSn_6 trigonal prisms at the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ site in A_3B -type “ Ca_3Sn ”, i.e., $(\text{Ca}_3\text{Sn})(\text{Rh}_4\text{Sn}_{12})$. It is worthwhile to note that Matthias’s empirical rule, a practical guideline most used decades ago, which proposes that T_c peaks at the valence-electron-

per-atom (e/a) ratios of ~ 4.7 and 6.4 , works pretty well for A15 compounds, with the highest T_c of 23.2 K observed in Nb_3Ge with an $e/a = 4.75$.^{125,1}

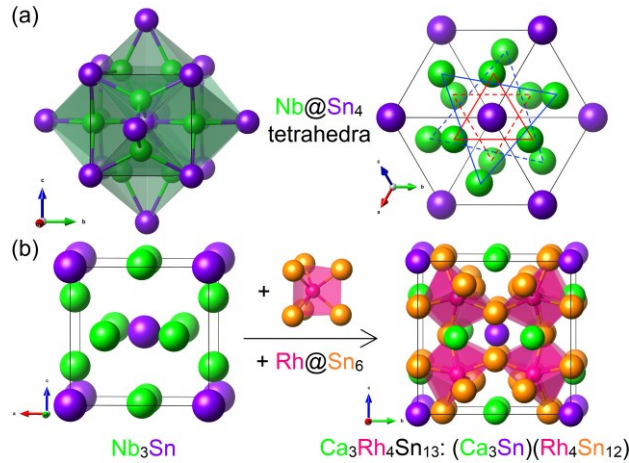


Figure 2 (a). Crystal structure of the A15 superconductor Nb_3Sn . Green and purple balls represent Nb and Sn atoms, respectively. **(b).** Structural relationship between Nb_3Sn and $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$. Pink and orange balls stand for inserted Rh and Sn atoms for $\text{Ca}_3\text{Rh}_4\text{Sn}_{13}$.

2.2. Chevrel Superconductors and their Relatives.

The fragment formalism can also be employed to understand another family of superconductors- Chevrel superconductors. Most Chevrel superconductors MMo_6X_8 ($\text{X} = \text{S}, \text{Se}, \text{Te}$) crystallize in a rhombohedral structure with an $R\bar{3}$ space group; very few of them adopt triclinic space group $P\bar{1}$ or hexagonal space group $P6_3/m$.^{126–129} However, a simple repeating unit can be found in all Chevrel phases, which is shown in Figure 3(b), generated from LaMo_6S_8 ($R\bar{3}$). The Mo atoms construct octahedron (i.e. a trigonal antiprism) surrounded by eight X atoms. The X_8 framework is very close to a simple cubic construction and beyond the Mo_6X_8 cluster, the M_8 framework is stacked as cubic-like type as well. With different interatomic distances between Mo atoms in different Mo_6 clusters and various lengths between Mo and nearest X atom in other X_8 clusters, Chevrel phase MMo_6X_8 materials can adopt in different unit cells. Almost half a century later, a new superconductor, $\text{K}_2\text{Cr}_3\text{As}_3$ was reported with $T_c \sim 6.1$ K, crystallized in a quasi-one-

dimensional structure very similar to the Chevrel phase structure.¹³⁰ Its crystal structure is shown in Figure 3(c). In hexagonal $K_2Cr_3As_3$ (space group $P-6m2$), along the c axis of the crystal, “infinite” quasi-one-dimensional (Q-1D) $[Cr_3As_3]^{2-}$ chains are running. The K atoms are located in between the Q-1D chains. Three Cr atoms within the ab -plane are stacked with three other Cr atoms in a staggered way, and the same pattern can be found for the As atoms. Thus, by viewing the crystal structure from the c axis, the As “pseudo-hexagonal rings” are encircling Cr “pseudo-hexagonal rings” and are stacked along the c axis, similar to the $[Mo_6X_8]^{2-}$ pattern shown in Figure 3(a).

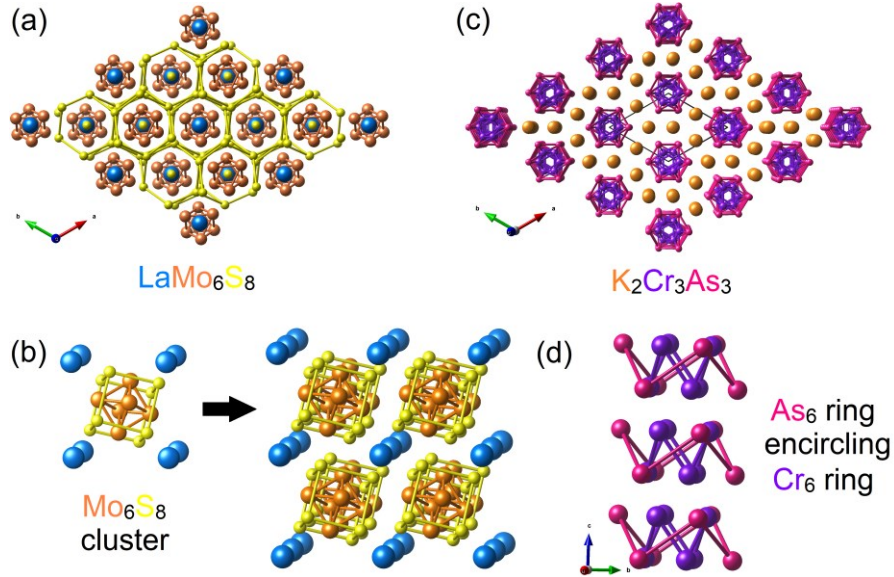


Figure 3 (a). Crystal structure of a Chevrel phase, LaMo₆S₈. Blue, orange and yellow balls represent La, Mo and S atoms, respectively. (b). Repeating units in S-based Chevrel phases with cubic arrangement. (c). Crystal structure of superconducting K₂Cr₃As₃ where orange, purple and pink balls stand for K, Cr and As atoms, respectively. (d). The Q-1D $[Cr_3As_3]^{2-}$ chain in K₂Cr₃As₃ with quasi-As₆-hexagonal rings encircling quasi-Cr₆-hexagonal rings.

2.3. *f-d* Interactive Polyhedra in Heavy-fermion Superconductors-Superconductivity Runs in Structural Families.

The rare-earth-based superconductor CeCu₂Si₂ surprised the community due to its distinct mechanism for forming superconducting Cooper pairs, the first of a family later called Heavy

Fermion Superconductors (HFSCs).^{34,131,132} From the viewpoint of physics, unconventional superconductivity should result from symmetry breaking in addition to gauge symmetry breaking.¹³³ To translate the concepts of physics into chemistry terms, we can simplify this as meaning that the emergence of superconductivity requires microscopic interactions besides electron-phonon interactions, such as strong electron-electron coupling and spin-fluctuations. Except for the discovery of unconventional superconductivity, the HFSCs also inspired physicists to reexamine the conventional quantum theory about the inner-shell electrons of an atom which are solely distributed due to Hund's rules to reduce the Coulomb repulsion.

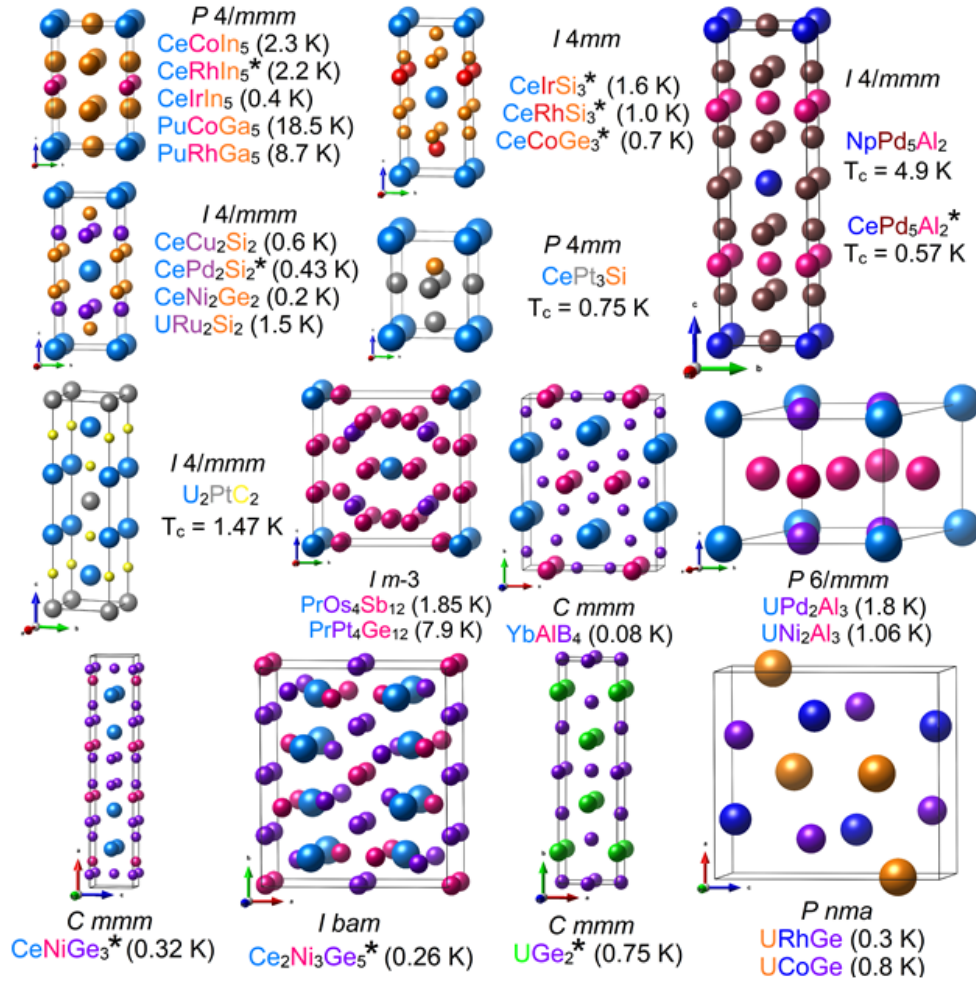


Figure 4. Crystal structures of representative HFSCs with their superconducting transition temperatures labeled. Asterisks indicate that superconductivity can only be induced by high pressure.

Until now, there are various HFSCs reported. The crystal structures of HFSCs are summarized in Figure 4 with their superconducting critical temperatures marked.^{34,134–173} Among them, in CePt₃Si, the silicon atoms are located in the void of a Pt@Pt₄ square pyramid while another Pt@Pt₄ square pyramid stacks along the *ab*-plane.¹⁵⁰ The Ce atoms occupy the voids in the Pt-Si framework, as shown in Figure 5(a). However, for CeMX₃ (M = Co, Rh, Ir; X = Si, Ge), the M and X atoms construct corner-shared M@X₅ square pyramids.^{137–139,155} Layered structural features can be related to the weak interaction between X atoms in different square pyramids. Identical to CePt₃Si, the Ce atoms in CeMX₃ occupy the “channel” center in the M-X frameworks, as illustrated in Figure 5(b). Superconductivity in CePt₃Si was observed below $T_c \sim 0.75$ K at ambient pressure. Interestingly, the material was found to be antiferromagnetically (AFM) ordered with a Néel temperature of 2.2 K which implies that the superconductivity coexists with AFM order below 0.75 K. However, in CeMX₃, the superconducting transition only appears under high pressure. Another remarkable HFSC is REMX₅ (RE= Ce and Pu; M= Co, Rh, Ir; X= In and Ga) in the space group of $P 4/mmm$, the structure of which is shown in Figure 5(c).^{135,146–149,173} In REMX₅, face-sharing RE@X₁₂ polyhedra construct REX₅ layers segregated by M layers. CeCoIn₅ was determined to become superconducting below $T_c = 2.3$ K,¹³⁵ which is a high value among HFSCs, while superconductivity in CeIrIn₅ was realized below $T_c = 0.4$ K. The study of CeCoIn₅ indicates the superconductivity is critical for the magnetic ordering. In addition to Ce-based REMX₅ compounds, several Pu-based superconductors have also been discovered, with extremely high critical temperatures among HFSCs, compounds such as PuCoIn₅ ($T_c = 2.5$ K),¹⁷³ PuCoGa₅ ($T_c = 18.5$ K)¹⁴⁸ and PuRhGa₅ ($T_c = 8.7$ K).¹⁴⁹

The only confirmed Yb-based heavy-fermion superconductor is β -YbAlB₄ which crystallizes in the orthorhombic $C mmm$ space group.¹⁵⁹ It consists of boron clusters made up of

edge-sharing boron heptagons and pentagons and Yb_2Al_2 quadrilateral stacking along the c axis. In 2008, $\beta\text{-YbAlB}_4$ was reported to be a superconductor with $T_c \sim 0.08$ K. From a chemistry perspective, superconductivity runs in structural families. Based on this empirical rule, a new type of superconducting quantum material $\text{Yb}_x\text{Pt}_5\text{P}$ with various Yb concentrations was discovered.¹⁷⁴ $\text{Yb}_x\text{Pt}_5\text{P}$ crystallizes in the anti- CeCoIn_5 type structure with the same space group, $P4/mmm$, as shown in Figure 5(c). A large heat capacity jump attributed to an antiferromagnetic ordering is observed below ~ 0.3 K for samples with both low-Yb and high-Yb contents. Moreover, a possible superconducting transition was observed as well below ~ 0.6 K for low-Yb-ratio samples, which is almost eight times higher than that of $\beta\text{-YbAlB}_4$. Further investigation will be needed to verify the superconductivity in this novel Yb-based quantum material.

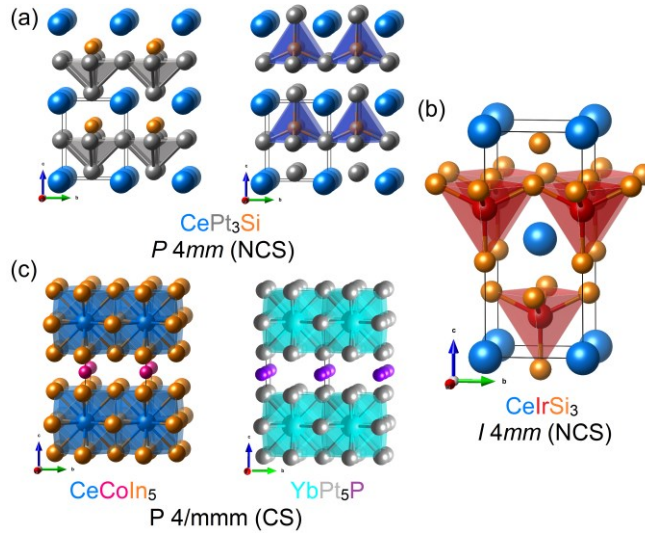


Figure 5. Crystal structures of (a) CePt_3Si ; (b) CeIrSi_3 ; (c) CeCoIn_5 and YbPt_5P with the emphasis on the f - d clusters. The space groups of each compound are marked where NCS and CS indicate non-centrosymmetric space group and centrosymmetric space group, respectively.

2.4. Cuprate Superconductors and Other Transition Metal Oxides.

Most cuprate superconductors derive from the perovskite structure, and in fact, perovskite structure compounds are probably the most studied types of compounds studied nowadays due to

their fascinating properties, which extend beyond superconductivity. Perovskites can generally be formalized as ABX_3 compounds, where A is usually an alkaline-earth or rare-earth element, B is a transition-metal element and X is an oxygen or a halide.¹⁷⁵ $BaBiO_3$ with the ABX_3 perovskite structure is a crucial parent compound for two important non-cuprate oxide superconductors, $BaPb_{1-x}Bi_xO_3$ ($T_{c-max} = 13$ K) and $Ba_{1-x}K_xBiO_3$ ($T_{c-max} = 30$ K).^{37,38} This crystal structure provides the structural platform to host a mixture of Bi^{3+} and Bi^{5+} , as well as charge density waves (CDWs) in $BaBiO_3$.^{176–178} The crystal structure of $BaBiO_3$ varies with temperature, as shown in Figure 6(a).¹⁷⁹ $BaBiO_3$ adopts to a cubic unit cell with the space group of $Fm\bar{3}m$ above ~ 820 K. When the temperature goes down, it transforms into $R\bar{3}H$ and maintains that structure until ~ 430 K. The symmetry of the compound keeps decreasing with lower temperature and results in monoclinic $I2/m$ (~ 430 K to ~ 140 K) and $P2_1/n$ (~ 140 K to 4.2 K (the lowest temperature for measurements)). Within the structural transformation, the $Bi@O_6$ octahedra tilt from the regular shape with the symmetry reducing from three C_4 axes ($Fm\bar{3}m$ and $R\bar{3}H$) to three C_2 axes ($I2/m$ and $P2_1/n$) to no high-symmetry axis ($P2_1/n$) (see Figure 6(b)). Moreover, there are always two distinctly crystallographic atomic sites for Bi atoms due to the nature of charge disproportion. Thus, two $Bi@O_6$ octahedra centered with different Bi sites arrange alternatively in the crystal lattice.

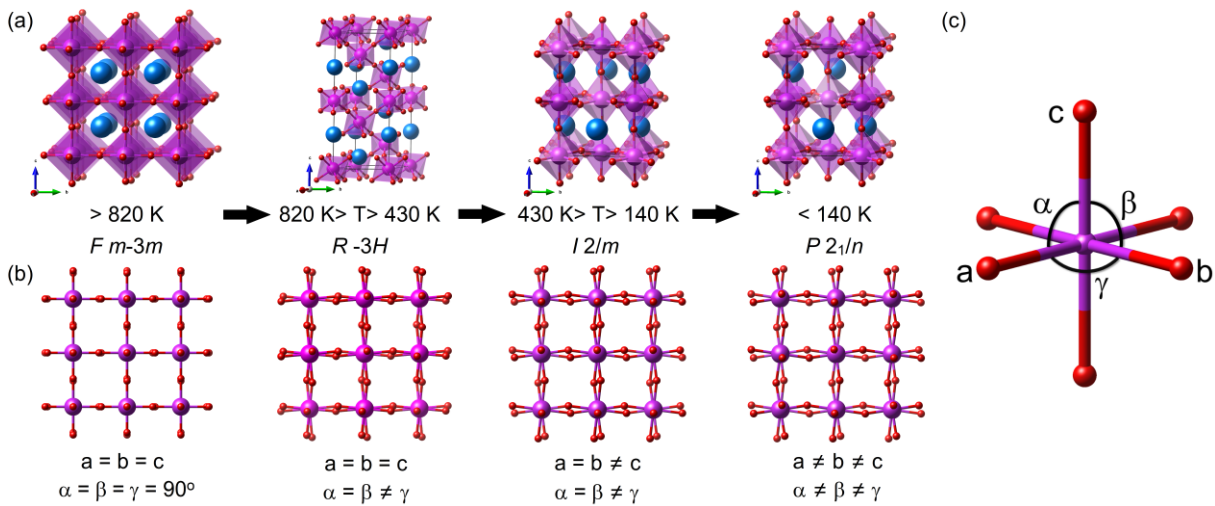


Figure 6. (a) Evolution of the crystal structure of BaBiO₃ with decreasing temperature. **(b)** The Bi-O frameworks in all structure types. The differences are defined by the notation marked in **(c)** where α , β , γ indicate the O-Bi-O bond angles and a , b , c represent the Bi-O bond lengths.

Most cuprate superconductors can be described by this general formula: $A_mE_2R_{n-1}Cu_nO_{2n+m+2}$ where $A = \text{Bi, Tl, Pb, Hg, Cu or RE}$; $E = \text{Ca, Sr, Ba or vacant}$; $R = \text{Ca, Y or RE}$; $m = 0, 1 \text{ or } 2$; $n = \text{positive integer}$. On the basis of the real crystal structures, this formula can be written as: $[(EO)(AO)_m(EO)] + \{(CuO_2)\}[R(CuO_2)]_{n-1}$ where $[(EO)(AO)_m(EO)]$ is called the charge reservoir block and $\{(CuO_2)\}[R(CuO_2)]_{n-1}$ is called the active block. Most cuprate superconductors crystallize in tetragonal unit cells. One can easily find that for tetragonal cuprate superconductors, the materials adopt the space group $I4/mmm$ when $m = 0$ or 2 , while the space group will be $P4/mmm$ when $m = 1$, see Figure 7 extracted from Ref. 66.⁶⁶ To name cuprate superconductors, there are three general notations, which are $m2(n-1)n$ corresponding to the m and n values in chemical formula as mentioned above. For example, $La_{2-x}Ba_xCuO_4$ (LBCO)³⁹ can be symbolized as 0201 since its chemical formula can be written as $(La(Ba)O)_2(CuO_2)$, which indicates that $m = 0$ and $n = 1$. Another widely used way for notation of different types of cuprate superconductors is the A atom followed by the atomic ratio of different elements; Y-123 for example represents the superconductor $YBa_2Cu_3O_{7-\delta}$, while the number for O atoms is always emitted. The third notation is to utilize the first letter of each elements' name, i.e., YBCO is the abbreviation of $YBa_2Cu_3O_{7-\delta}$. By looking at the two blocks constructing cuprate superconductors, the superconducting current was determined to flow in the active block, with the CuO_2 layers, while the doping normally happened in the charge reservoir block. Here, we will briefly introduce the structural features of major types of cuprate superconductors with their basic superconducting properties. A more detailed summary can be found in review article by Chu et. al.⁶⁶

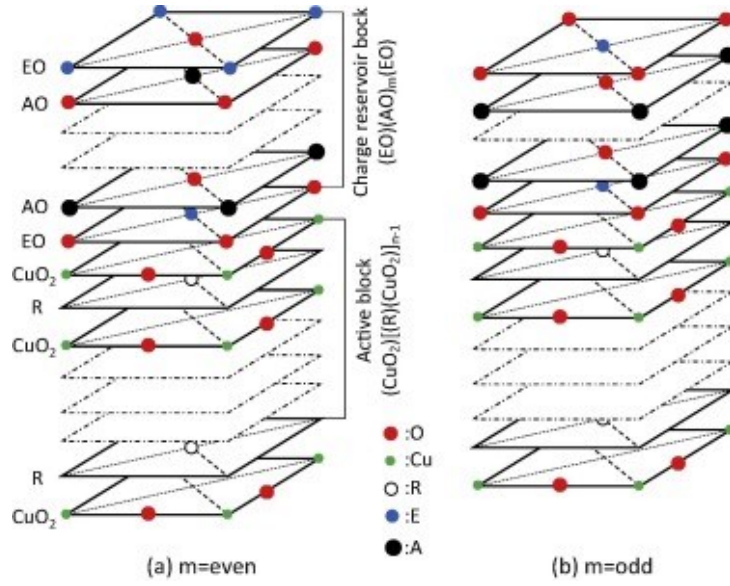


Figure 7. The general structure for cuprate SCs $A_mE_2R_{n-1}Cu_nO_{2n+m+2}$ when (a) m = even and (b) m = odd. Reprinted with permission from Ref.66. ⁶⁶ Copyright [2015] [Elsevier B.V.].

As the first group of cuprate superconductors realized, LMCO was derived from Ba-doped La_2CuO_4 and grew into a big family over the years, including $(R, M)_2CuO_4$ ($R = La, Pr, Nd, Sm, Eu$; $M = Ca, Sr, Ba, RE$), La_2CuO_{4+x} , Sr_2CuO_{3+x} , $(Sr,Ba)CuO_{3+\delta}$ etc.^{40,180–195} The crystal structures of 214-type LMCO show three distinct types when R and M vary. As shown in Figure 8(a), $(La, AE)_2CuO_4$ ($AE =$ alkali metals), Sr_2CuO_{3+x} and $(Sr,Ba)CuO_{3+\delta}$ crystallize in the same structure type in the space group of $I4/mmm$ while there are vacancies on different oxygen sites for different compounds, i.e., oxygen has vacancies on the O1 site for Sr_2CuO_{3+x} while on the O2 site for $(Sr,Ba)CuO_{3+\delta}$. However, for other $(R, M)_2CuO_4$ superconductors, such as $(Nd, Sr, Ce)_2CuO_4$ and $(Nd, Ce)_2CuO_4$, the crystal structures are similar but not identical. The former one adopts the $P4/nmm$ space group with $Cu@O_5$ pyramids instead of $Cu@O_6$ octahedra shown in $(La, AE)_2CuO_4$. Furthermore, in $(Nd, Ce)_2CuO_4$, the CuO_2 layers are well separated from other oxygen layers and construct $Cu@O_4$ square planes. Superconducting La_2CuO_{4+x} was found to crystallize in the orthorhombic space group $Cmca$ where “distorted $Cu@O_6$ octahedra” with the splitting of oxygen

sites can be found. Extra oxygen was also found to occupy a new atomic site with small occupancy.¹⁹⁶ Superconductivity was observed in LBCO at 28 K. Further study on Sr-doped La_2CuO_4 (LSCO) showed that LSCO exhibited superconductivity below $T_c = 38$ K while this value was increased to 52 K under 1.68 GPa of applied pressure.¹⁸¹ Other 214-type superconductors became superconducting with even higher critical temperatures, such as $\text{La}_2\text{CuO}_{4+x}$ ($T_c \sim 40$ K)¹⁹⁷ and $\text{Sr}_2\text{CuO}_{3+x}$ ($T_c \sim 94$ K)¹⁹³.

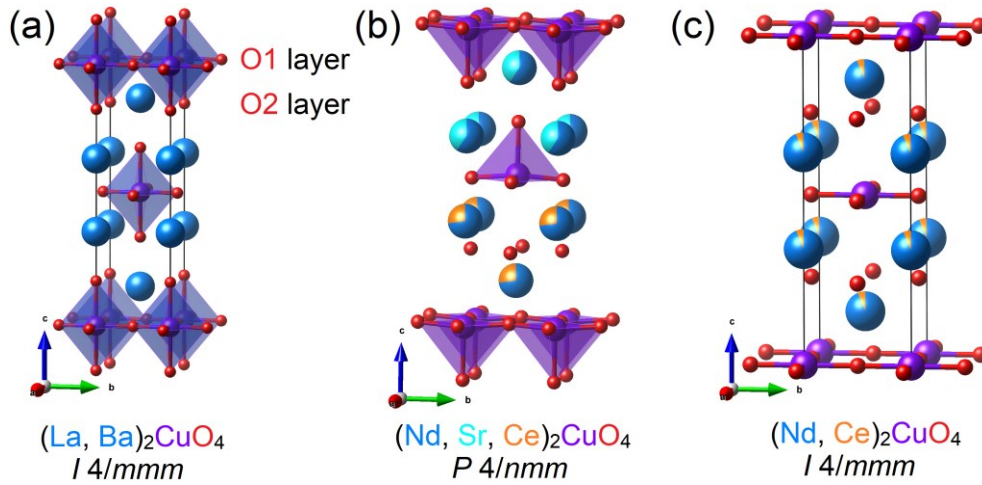


Figure 8. Crystal structures for (a) $(\text{La, Ba})_2\text{CuO}_4$; (b) $(\text{Nd, Sr, Ce})_2\text{CuO}_4$ and (c) $(\text{Nd, Ce})_2\text{CuO}_4$.

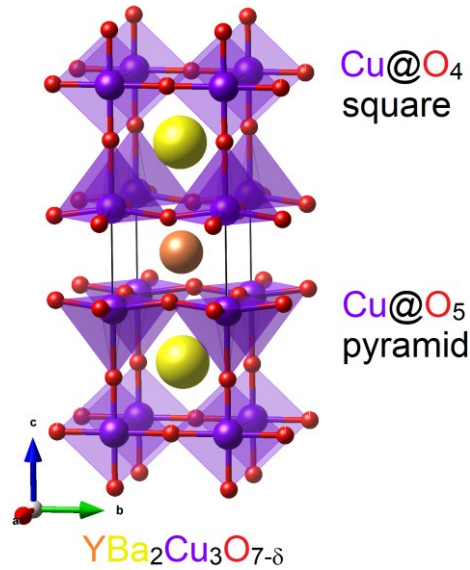


Figure 9. Crystal structure of YBCO where orange, yellow, purple and red balls represent Y, Ba, Cu and O atoms, respectively.

After the discovery of the LBCO superconductor, a cuprate superconductor was discovered by M.K. Wu, C.W. Chu and coworkers in 1987 with a T_c above the liquid N_2 boiling temperature (77 K), later shown to be Y-123.⁴⁰ The most representative compounds in this family are $RBa_2Cu_3O_{7-\delta}$ where $R = Y, La, Nd, Sm, Eu, Gd, Ho, Er, \text{ and } Lu$.^{41,42} The crystal structures are presented in Figure 9. $RBa_2Cu_3O_{7-\delta}$ crystallizes in an orthorhombic cell with the space group of $Pmmm$ according to low-temperature neutron diffraction. The Y atom in the body-center site was found to be sandwiched by two layers of CuO_2 constructing an active block. CuO layers and BaO layers are located at the top and bottom of the unit cell as the charge reservoir block. The superconducting transition temperature was found to be 92 K for Y-123 while other materials with R being appropriate lanthanides display T_c s ranging from 91 to 95 K. Later, Maeda et al. synthesized $Bi_2Sr_2CaCu_2O_8$ ('BSCCO') found it to be superconducting at ~ 84 K.⁴³ Later, extensive studies were performed on this new group of superconductors and found that the major members could be described as $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ where n is positive integer. The Bi-based cuprate superconductors include five major types of compounds, which is a perfect example showing how crucial the CuO_2 layer is to superconductivity. Moreover, BSCCO superconductors are the first group of materials exhibiting critical temperatures up to 110 K without rare-earth elements. Increasing superconducting transition temperatures can be found with raising n value. When $n=1$, the Bi-2201 compound was found to be superconducting below $T_c \sim 28$ K while Bi-2212 ($n=2$), Bi-2223 ($n=3$) and Bi-2234 ($n=4$) were observed superconducting below T_c s = 96 K, 110 K and 90 K, respectively.⁴⁴⁻⁴⁷ As we mentioned at the beginning of the cuprate superconductors' section, n represents the amount of CuO_2 layers. Since CuO_2 layers are crucial for the superconductivity, we can clearly see in BSCCO superconductors that when more CuO_2 layers are "inserted", the T_c s increase a lot, from 28 K to 110 K. However, when $n=4$ the T_c drops

to 90 K, which has been attributed to the electrostatic shielding and proximity effect from CuO₂ layers or the depletion of charge from the central layers. BSCCO superconductors crystallize in space group $I 4/mmm$. From the crystal structure shown in Figure 10, we can clearly see how additional CuO₂ layers are inserted into BSCCO compounds and how these changes the structure in general. Tl and Hg, as heavy elements with fatal toxicity, were utilized to produce higher temperature cuprate superconductors. Similar general formulas were given for both TBCCO and HBCCO with BSCCO: $Tl/Hg_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$.^{48–65} Here we are going to introduce three groups of materials: TBCCO when $m = 1$ ($n = 1, 2, 3, 4, 5$), TBCCO when $m = 2$ ($n = 1, 2, 3, 4$) and HBCCO when $m = 1$ ($n = 1$ to 7). The crystal structures are shown for TBCCO superconductors since HBCCO ($m = 1$) crystallize into the same structure type as TBCCO when $m = 1$. As mentioned, when $m = 1$ the materials adopt into $P 4/mmm$ space group and $I 4/mmm$ for $m = 2$. The crystal structures are shown in Figure 11. Similar with BSCCO, with larger n values, the critical temperatures increase a lot at the beginning for both groups while T_c s start to drop after reaching a maximum: for TBCCO when $m = 1$, T_c increases from below 40 K ($n = 1$) to 82 K ($n = 2$) to 116 K ($n = 3$) to 122 K ($n = 4$) and decreases to below 100 K ($n = 5$); for TBCCO when $m = 2$, T_c increases from 90 K ($n = 1$) to 110 K ($n = 2$) to 125 K ($n = 3$) and decreases to 104 K ($n = 4$); for HBCCO when $m = 1$, T_c increases from 95 K ($n = 1$) to 114 K ($n = 2$) to 133 K ($n = 3$) and decreases to 125 K ($n = 4$) and 110 K ($n = 5$) and 107 K ($n = 6$) and below 90 K ($n = 7$). This further confirms the significance of CuO₂ layers to superconductivity and reveals that by simply inserting more CuO₂ layers into typical system, the critical temperature will finally reach a maximum.

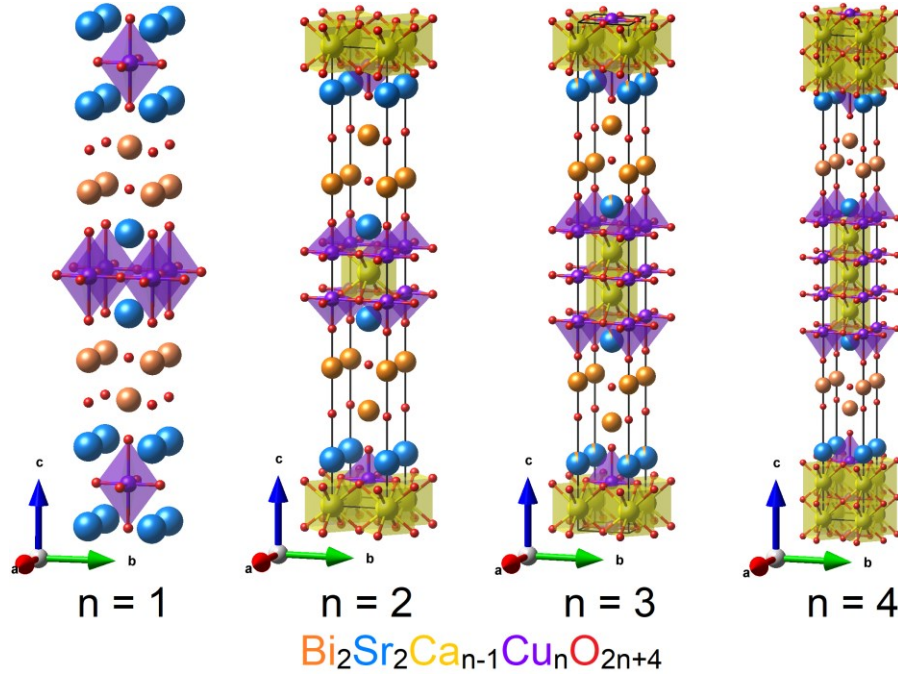


Figure 10. Crystal structures of BSCCO superconductors when $n = 1 - 4$ where orange, blue, yellow, purple and red balls stand for Bi, Sr, Ca, Cu and O atoms, respectively.

Interestingly, superconductivity was also discovered in metal-rich compounds with anti-perovskite structures such as MgXNi_3 ($\text{X} = \text{B}, \text{C}, \text{and N}$)¹⁹⁸, La_3InO_x ^{199,200}, $\text{Sr}_{3-x}\text{SnO}$ ²⁰¹, $\text{Li}_2\text{Pt}_3\text{B}$ ²⁰² and APt_3P ²⁰³ compounds. In 2001, He et al. discovered the superconductivity in anti-perovskite MgC_xNi_3 ($0.5 > x > 1.25$), below $T_c \sim 8.5$ K for the MgCNi_3 . This novel Ni-rich superconductor crystallizes in primitive cubic space group $P m\bar{3}m$, as shown in Figure 12. The vertex-shared C@Ni_6 octahedron is located in the center of the cubic cell while Mg atoms occupy the corners. Unlike the bismuthate superconductors, MgCNi_3 hosts a stable crystal structure without any structural phase transition over the temperature range from 2 to 295 K.²⁰⁴ Moreover, no structural phase transition was observed under high pressure up to ~ 32 GPa.²⁰⁵ The high Ni contents drove the community to study the possible magnetic contribution to the superconductivity and examine whether MgC_xNi_3 is an unconventional superconductor. Theoretical calculations on MgCNi_3

suggested that the $3d$ states from the Ni atoms dominate at the Fermi level while a von Hove singularity is observed just below the E_F .^{206,207} In 2012, Kumar et al. combined experimental and theoretical efforts and figured out that superconducting MgCNi_3 is in proximity of ferromagnetism and is a moderately-coupled BCS superconductor with an electron-phonon coupling constant λ of 0.69.²⁰⁸ Moreover, a family of ternary platinum phosphides APt_3P ($A = \text{Ca}, \text{Sr}$ and La) with an anti-perovskite structure was discovered to be strong coupled BCS superconductors.²⁰³

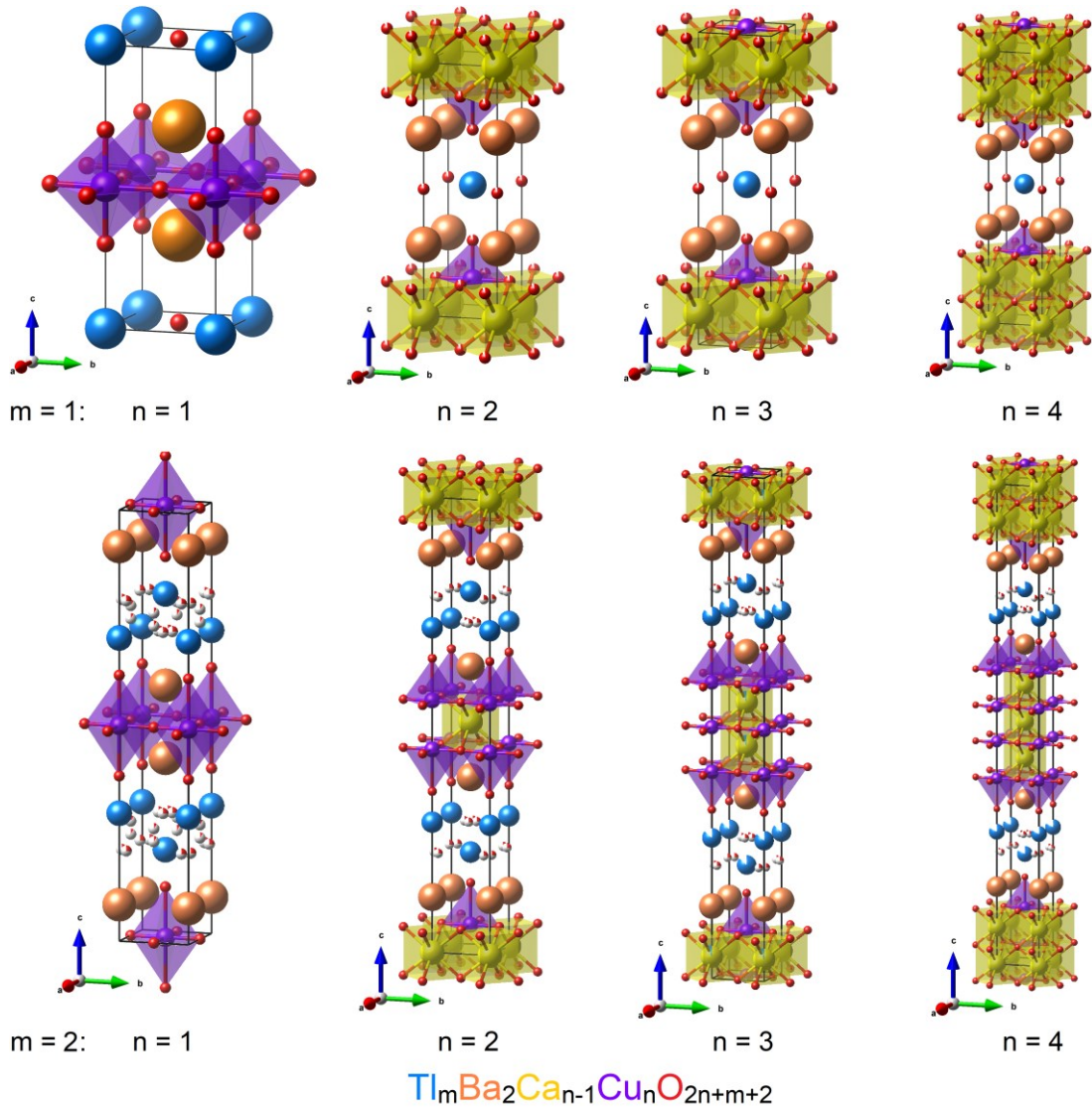


Figure 11. Crystal structures of TBCCO superconductors when $m = 1$ & 2 ; $n = 1 - 4$ where blue, orange, yellow, purple and red balls stand for Tl, Ba, Ca, Cu and O atoms, respectively.

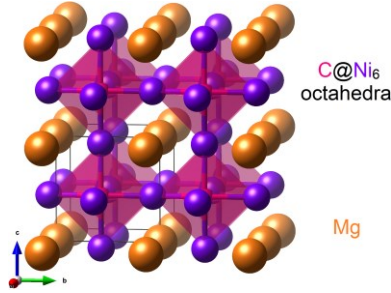


Figure 12. Crystal structure of MgCNi_3 where orange, purple and red balls stand for Mg, Ni and C atoms, respectively.

2.5. Iron-based High- T_c Superconductors (IBSCs).

As discussed previously, the existence of magnetic elements, like Fe, is supposed to interfere with electron-phonon coupling and thus result in the failure to induce superconductivity due to their effect on the formation of Cooper pairs. Although there were some early reported Fe-containing superconductors, for instance, $\text{Lu}_2\text{Fe}_3\text{Si}_5$ ²⁰⁹ and Th_7Fe_3 ²¹⁰, the superconductivity was not attributed to the $3d$ electrons of Fe in such compounds. This situation changed in 2006 when Kamihara et al. reported superconductivity in LaOFeP below $T_c \sim 4$ K.⁸⁵ Subsequently, related superconductors were reported for LaNiOP ($T_c = 3$ K)⁸⁶ and the high- T_c superconductor $\text{LaFeAsO}_{1-x}\text{F}_x$ ($T_{c-\text{max}} = 26$ K) in 2008⁸⁴. Fe-based superconductors with critical FeM_4 ($M = \text{As}$ and Se) layers can be sorted into four major categories as follows: 1111-type (e.g. $\text{LaFeAsO}_{1-x}\text{F}_x$), 122-type (e.g. $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$, $\text{Sr}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$), 111-type (e.g. LiFeAs , Na_xFeAs) and 11-type (e.g. Fe_{1+x}Se). The stripe antiferromagnetic spin-density-wave (SDW) order coinciding with the structural transition at high temperature, in general, is believed to hold the key to induce the superconductivity upon chemical substitution or under high pressure.

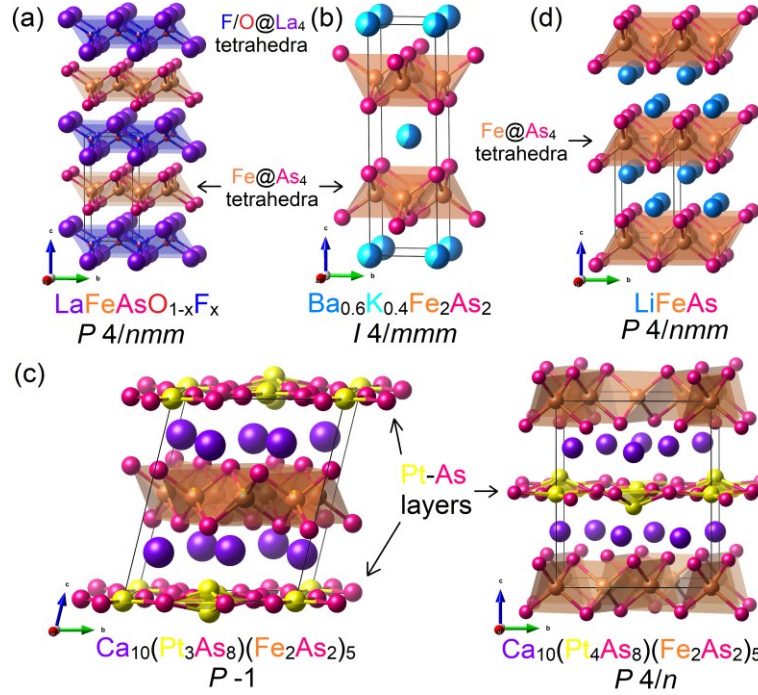


Figure 13. Crystal structures of representative IBSCs in (a) 1111 type; (b) 122 type; (c) 10-3-8/10-4-8 types; (d) 111 type.

Superconductivity in the 1111-type structure (abbreviated as 1111 in the following) was the first reported in this family, and included two superconductors mentioned above, LaFePO and LaFeAsO_{1-x}F_x, with fluorine/hydrogen-doped REFeAs(O, F/H) (RE = La, Ce, Sm etc.) and oxygen-deficient REFeAsO_{1-x} (RE = La, Nd, Sm etc.) found subsequently^{84,85,89-92} The crystal structure for 1111 is shown in Figure 13(a) where one can find edge-shared Fe@As₄ layers separated by the O(F/H)@RE₄ layers. The two distinct layers are aligned well and stacked along the *c* axis of the crystal. Superconducting phases of 1111 crystallize in a tetragonal unit cell with space group *P* 4/*nmm*. So far, the highest *T_c* in 1111-type has been observed in Gd_{0.8}Th_{0.2}FeAsO with *T_c* = 56 K in 2008⁹⁰. Another major member is 122-type IBSCs (IBSC = iron based superconductor, with the materials with the structure of interest here abbreviated as 122 below) can be summarized as AE_{1-x}A_xFe₂As₂ (AE = alkaline earth, A = alkali metal) and AE(Fe_{2-x}TM_x)As₂ (TM = transition metals).⁹⁴⁻¹⁰⁶ The crystal structures of superconducting 122 phases can be traced

back to lanthanide-based quaternary borocarbides (RT_2B_2C , $R = \text{Sc, Y, La, Tm, Er, Ho, Dy, Th, Pr, Nd, Gd, Tb and Lu}$; $T = \text{Ni, Pd, Pt, Co, Rh, Ir, Os, Ru and Re}$).^{211,212} Both 122-type IBSCs and lanthanide-based quaternary borocarbides crystallize in a tetragonal unit cell with body-centered space group of $I4/mmm$. In lanthanide-based quaternary borocarbides, B-C-B can be treated as a chemical unit just like As-As can in $BaFe_2As_2$, as shown in Figure 13(b). In 2008, $Ba_{1-x}K_xFe_2As_2$ was reported to host superconductivity by Rotter et al. with the $T_c \sim 38$ K when $x \sim 0.4$.⁹⁴ The parent compound $BaFe_2As_2$ itself was found to host a spin-density-wave (SDW) below 140 K accompanied by a structural phase transition from tetragonal $I4/mmm$ to orthorhombic $Fmmm$.²¹³ Moreover, incorporating other effective fragments with FeAs layers can lead to the discovery of new superconductors, for example 10-3-8 $Ca_{10}(Pt_3As_8)(Fe_2As_2)_5$ and 10-4-8 $Ca_{10}(Pt_4As_8)(Fe_2As_2)_5$ superconductors¹¹⁵, as can be seen in Figure 13(c). In 111-type IBSCs there were two typical examples, which are Li_xFeAs and Na_xFeAs - superconductivity can be observed at ambient pressure in Li_xFeAs ^{107,108} and Na_xFeAs ¹⁰⁹. 111-type compounds crystallize in a primitive tetragonal unit cell with the space group of $P4/nmm$ (Figure 13(d)). Similar with other IBSCs, FeAs layers are also the prominent feature in 111s while alkali metals are intercalated in between. The 11-type IBSCs are the only family of compounds which contain Fe-Ch ($Ch = S \& Se \text{ or Te}$ -substituted S/Se) layer instead of Fe-As layers.^{110,111,214-217} Even though they exhibit relatively lower T_c among IBSCs, the easiness of their fabrication and the large enhancement of T_c with applied pressure are intriguing. 11-type IBSCs crystallize in tetragonal cell with space group of $P4/nmm$, where the Fe-Ch layers simply stack along the c axis. Superconductivity was found in bulk FeSe crystal in 2008 with $T_c = 8$ K. Later, a great enhancement on T_c of FeSe was achieved by one unit-cell-thick FeSe films grown on Se-etched $SrTiO_3(001)$ substrate with $T_c \sim 53$ K.¹¹¹ Moreover, when applying high pressure on $Fe_{1.01}Se$, a structural phase transition from tetragonal to NiAs-

type hexagonal phase (Figure 13(e)) could be found while superconductivity can exhibit in a wide pressure range. Note that NiAs is not a superconductor down to 1.3 K.²¹⁸ However, when the crystal structure was gradually transformed into a hexagonal cell, superconductivity could not be observed as a result.²¹⁹

The investigation of unconventional superconductivity in systems like IBSCs and cuprate SCs can usually be summarized in phase diagrams referencing to how electron/hole-doping affects physical properties such as magnetic ordering and superconductivity, and their relationships. Figure 14(a)²²⁰ shows a schematic phase diagram for 122-type IBSCs with electron/hole-doping. One can find that superconductivity emerges at the vicinity of stripe magnetism from orthorhombic phase of 122-type parent compounds of IBSCs. The insets show the temperature-dependence of nematic (ϕ) and magnetic (M) order parameters, which, due to their primary interest in materials physics, are not going to be discussed in this review. Similar with IBSCs, in the LMCO cuprate superconductors it was realized that the superconductivity could be achieved by doping their parent compounds, which are Mott insulators. Mott insulators are a type of material that are supposed to be electrically conductive based on conventional band theory but instead behave as insulating due to electron-electron interactions. Figure 14(b)²²¹ shows a general phase diagram for LMCO, which is more or less applicable to all cuprate superconductors. In the left side of Figure 14(b) shows the hole doping of Mott insulator parent compound La_2CuO_4 . With small doping of Sr, the material maintains an antiferromagnetic Mott insulating state. When the concentration of Sr increases, after experiencing a spin-glass (SG) state, superconductivity is induced. Similar behavior can be found on the electron doping side of the phase diagram except that the AFM state persists for a larger doping range and can coexist with superconductivity within a narrow doping range. Such behavior

for cuprate superconductors is comparable to that of HFSCs where the magnetic order can always interact/coexist with superconducting states.

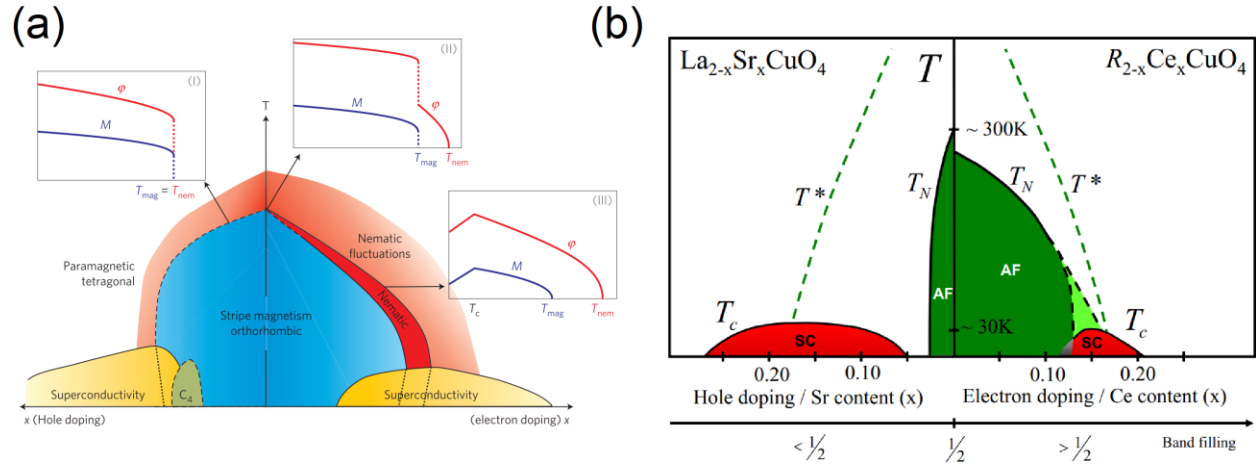


Figure 14. (a) Schematic phase diagram of the 122-type BaFe_2As_2 superconducting family, where the blue region indicates stripe magnetism in an orthorhombic phase. Superconductivity is shown as a yellow region. The red area stands for strong nematic fluctuations. The insets show the temperature-dependence of the nematic (ϕ) and magnetic (M) order parameters. Reprinted with permission from Ref. 220. Copyright [2014] [Springer Nature]. **(b)** Phase diagrams of LSCO and NCCO systems. SC, AF, T_c , T_N and T^* represent superconducting phase, antiferromagnetic ordered phase, superconducting transition temperature, antiferromagnetic ordering transition temperature (Néel temperature) and approximate extent of pseudogap phase. A spin-glass phase should also exist at the low hole doping region, which is not shown. Reprinted with permission from Ref. 221. Copyright [2010] [American Physical Society].

3. Approaches to New Superconductors

3.1. Chemical Bonding and Electron Counts in Superconductivity.

Most superconductors can be sorted into two categories based on whether their superconducting mechanism can be explained by BCS theory or not: generally referred to as conventional and unconventional superconductors, based on whether their superconducting mechanisms can be explained by BCS theory or not. Most discovered superconductors are conventional superconductors and can be explained by a BCS mechanism. There also exist many unconventional ones, such as heavy-Fermion superconductors (HFSCs), cuprate superconductors, organic superconductors, quaternary borocarbide superconductors, iron-based superconductors (IBSCs), twisted bilayer graphene superconductors (TBGSCs)²²² etc (listed in the order of discovery date). BCS theory was proposed to explain the microscopic mechanism of conventional superconductors in which electron and electron are mediated by phonon, i.e., weak-coupling BCS superconductors. So far, no general theory can be used to explain unconventional superconductors.

The “paired electrons” called Cooper pair, referring to BCS theory in section 1, in physics is known to the chemist: An electron pair, commonly symbolized by a line between two atoms in a chemical bond, depicts an “approximation” of the Cooper pair. One thing worth noting is that the coherence lengths, i.e., that can be intuitively interpreted as the “distance” of Cooper pairs, thus, the size of Cooper pairs, in high- T_c superconductors correspond to a few atomic radii, which indicates local approaches (chemical bonding pictures) may become more relevant. The normal state of a metal becomes unstable when an attractive exchange interaction occurs between the conduction electron, but opposite in superconducting state. Understanding the origins of the attraction in terms of chemical bonding, therefore, opens the door to learning about the chemical prerequisites for superconductivity. It is possible to show that the process of Cooper pair formation

in superconductors can be chemically rephrased in terms of bonding, nonbonding, and antibonding interactions. This strategy was identified by Burdett, Simon et al. For example, Simon demonstrated that a detailed examination of the C-C bond in superconductors, which is so familiar to every chemist, indicated that it can induce superconductivity.³¹

Furthermore, by explaining chemical bonding interactions, electron counting works well as a formalism for classifying compounds and predicting the stability of new compounds. Simple ionic compounds can be explained by octet rules through which the electronegative element accepts electrons from the electropositive element to reach a closed-shell electron configurations for both elements. More complex compounds like boron cluster compounds can be interpreted using the Wade-Mingos polyhedral skeletal rules.^{223,224} Hume-Rothery rules²²⁵ are employed to explain the electronic structures of multi-shelled clustering γ -brass phases. The electron counting rules and the bonding schemes allow us to determine a structure's preferred electron count for most compounds in a very straightforward way without complicated first-principle calculations. Skutterudites are one of the most well-known class of Zintl compounds, which are intriguing in the materials science community because they can be members of various functional families such as thermoelectrics, heavy-fermion compounds and non-Fermi liquids. The Skutterudite family is derived from the mineral skutterudite, CoAs_3 . They can be generally formulized as BX_3 , where B is a transition metal element such as Fe, Co, Rh or Ir and X is a pnictogen such as P, As or Sb. They crystallize in cubic space group $I\bar{m}3$. The structural feature of skutterudites are the distorted square X_4^{4-} polyanions. Thus, CoAs_3 can be understood as $\text{Co}^{3+}_4(\text{As}_4)^{4-}_3$. Further, filled skutterudites with electron counts different from the electron-precise values have been made based on group 8 elements. In these cases, superconductivity can occur, for example, in $\text{LaRu}_4\text{As}_{12}$.²²⁶ Besides, skutterudites $\text{PrM}_4\text{X}_{12}$, $\text{PrOs}_4\text{Sb}_{12}$ and $\text{PrPt}_4\text{Ge}_{12}$ are also heavy-fermion

superconductors.^{227–229} The tilted corner-shared $M@X_8$ octahedra form the basic framework with Pr atoms inserting into the voids between the octahedra.

A distinctive way to count electrons is applied to the transition-metal complex systems such as the endohedral gallide superconductors. For example, $ReGa_5$,²³⁰ a Ga-cluster superconductor, contains 11 bonding orbitals per formula unit, and all these orbitals are fully occupied by 22e- (Re: 7e- from 5*d* and 6*s* orbitals + 5Ga: 3e- from 4*s* and 4*p* orbitals), thus the Fermi level of $ReGa_5$ should be located in a gap or pseudogap in the DOS. According to the WIEN2k calculation, small values of density of states, $N(E_F)$, are observed, which indicates stable electronic structures in the reciprocal space. The electron counting rules are not only used by chemists to evaluate the stability ranges of complex intermetallic compounds with specific structures, but also by physicists to estimate the superconducting transition temperatures in alloys. According to the BCS qualitative expression, a larger density of states at Fermi level $N(E_F)$ or larger electron-phonon interaction or both leads to a higher critical temperature for superconductivity (T_c). An empirical electron counting method has been generated by Matthias, stating that the number of valence electrons in a superconductor effectively affects T_c .¹ For the transition-metal-rich compounds with simple crystal structures or alloys, the maximal T_c occurs at approximately 4.7 and 6.5 valence electrons per atom, which has been validated on A15, α -Mn type and Laves phases. Taking the new superconductor $(Zr/Hf)_5Sb_{2.5}Ru_{0.5}$ for example, its valence electron concentration is calculated as follows: $(4 \text{ e-}/Hf \text{ or } Zr \times 5 \text{ Hf or } Zr + 5 \text{ e-}/Sb \times 2.5Sb + 8 \text{ e-}/Ru \times 0.5Ru)/8 = 4.6 \text{ e-}/\text{atom}$.^{231,232,233} Similarly, 6.5 e-/atom works for α -Mn type Re_6Zr .²³⁴ Since increasing the T_c in superconductivity by inducing a higher DOS at the Fermi level poses a high risk of destabilizing the compounds, from the viewpoint of chemistry, BCS-like superconductors inherit the conflict of structural stability (i.e lattice instability in physicists' terms) and

superconducting critical temperatures, which could be analogous to what occurs in thermoelectric materials with phonon-glass versus electron-crystal properties.

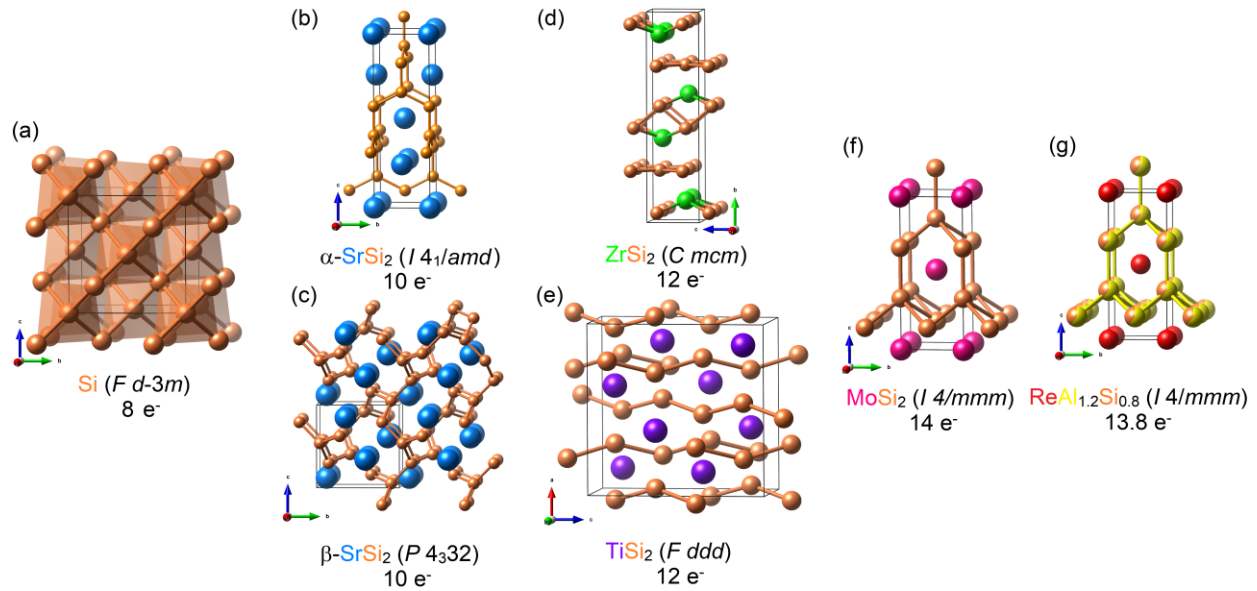


Figure 15. The structural and electronic links in the binary silicides.

To increase the chance of superconductivity, we can increase the instability of electronic structures. For example, tetragonal SrSi₂-type compounds related to cubic Laves phases, potentially good for superconductivity, can be interpreted by electron counting rules.^{235,236} The Fermi level for SrSi₂ is in the deep gap in the DOS. The integrated DOS up to the Fermi level gives the 10 e⁻ per SrSi₂. Replacing Sr with La will increase one electron per formula unit to lift the Fermi level from the deep gap to a peak in the DOS and drive an instability in the electronic structure, which may induce superconductivity. Interestingly, LaSi₂ has been proved to be a superconductor with $T_c = 2.3$ K.²³⁷ In addition to SrSi₂, which can be interpreted by the 10 e⁻ rule, more TM₂ (T: electropositive elements; M: main group elements) compounds can also be interpreted by other empirical electron rules. Take the TSi₂ system as an example, shown in Figure 15, silicon as a metalloid adopts the diamond structure by forming four bonds with its neighboring silicon atoms as illustrated in Figure 15(a). The combination of the alkali earth metals and main

group elements like Si has resulted in the discovery of many new Zintl phases, in which frameworks of main group elements accept the electrons donated by the alkali-earth metals to satisfy their valence requirements.²³⁸ The large electronegativity difference between Sr and Si makes both α - and β - SrSi_2 valence-precise semiconductors.

Structurally, the Si atoms in SrSi_2 form Si^- by forming three bonds with other Si atoms and two lone pair electrons by accepting one electron from the Sr atom. After replacing alkali-earth metals with early transition metals (T), the electronegativity differences between T and Si are smaller than those between the alkali-earth and Si, and the semiconducting band gap diminishes-- sometimes to zero - to yield metallic conductivity but with deep pseudogaps marking the preferred electron counts. ZrSi_2 , shown in Figure 15(d), contains a 4-connected Si^0 net and a ZrSi zig-zag planar sheet, which results in 12e- per ZrSi_2 in total (4e- per Si and 8e- per ZrSi). In another case, TiSi_2 , Si atoms can be considered as forming a zig-zag $(\text{Si}_2)^{4-}$ chain by accepting 4 electrons from the Ti. Similarly, it can be assumed that the Mo atom contributes 6e- to 2 Si atoms to form $(\text{Si-Si})^{6-}$ pairs in MoSi_2 . Thus, even numbers of electrons like 10e-, 12e-, 14e- and 18e- are favored for structural stability. On the other hand, odd numbers of electrons like 11e-, 17e- and 19e- are likely to correspond to the peaks instead of to (pseudo)gaps in the Density of States (DOS), which may lead to unstable electronic structures, and sometimes superconductivity, as shown in Figure 15(g) where $\text{ReAl}_{1.2}\text{Si}_{0.8}$ (13.8 e-) was determined to be superconducting below $T_c \sim 3.5$ K.²³⁹ Many well-known examples can be found such as YGe_2 (11e-) with a similar framework as ZrSi_2 , YGa_2 (9e-) with a similar framework as SrSi_2 and so on. The electron counts scheme gives a straightforward qualitative understanding of bonding in a wide variety of intermetallic compounds of metalloid elements. Moreover, a tremendous number of crystal structure types, seemingly

unrelated to each other, may be interpreted using the unifying concept of electron-rich multi-center bonding maps.

Another example is applying Wade-Mingos rules for boron compounds to tune their crystal structures and induce superconductivity. The B₂ dimer, B₃-trimer and B_{*n*}-framework provide metal borides with complex structural networks. The most famous example is MgB₂ with T_c ~ 39 K. A simple layered-honeycomb boron framework is the prominent structural feature in MgB₂.⁸³ The hexagonal Mg layers are well separated by boron honeycomb layers, as shown in Figure 16 (a). Another example is superconducting RERh₄B₄ (RE = Y, Nd, Sm, Er, Tm, Lu and Th).³² The crystal structure of RERh₄B₄ which crystallizes in a tetragonal space group *P* 4₂/*nmc* is shown in Figure 16 (b). Boron atoms in the form of B₂ dimers separate into two types that are located along either the *a* or *b* axis. Similar behavior can be found for Rh-Rh chains. Basically, the RE atoms create segregation for every two layers of Rh-Rh chains, together with coplanar B₂ dimers. The elongating direction of Rh-Rh chains is always orthogonal to the B₂ dimers, that is, when the Rh-Rh chains are along the *a*-axis, the coplanar B₂ dimers are located along the *b*-axis, and vice versa. As the Rh-Rh framework and B-B dimers become less segregated and boron dimers orient in four directions while the Rh atoms form a complex three-dimensional framework, the crystal symmetry of RERh₄B₄ changes to *I*4₁/*acd*. As a result, the superconducting T_c is lower.

The flexible arrangements of born atoms in intermetallics can be used to tune the crystal structures and thus govern the physical properties, such as superconductivity. For example, the B₂ dimers in the superconducting TaRh₂B₂ are critical for stabilizing the compound, surrounding the Ta atoms to form a chiral structure (*P* 3₁).²⁴⁰

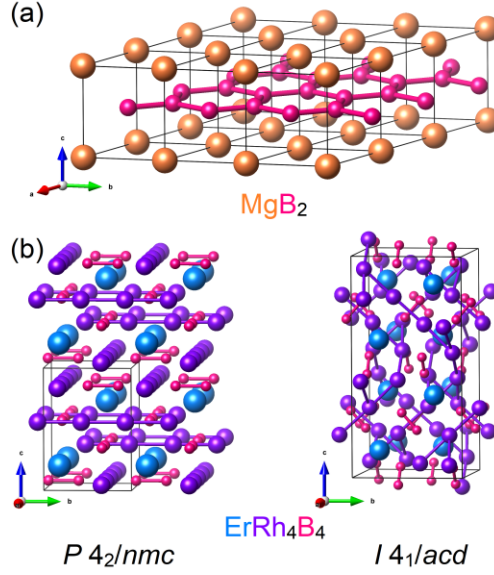


Figure 16. Crystal structures of borides superconductors: **(a)** MgB_2 ; **(b)** ErRh_4B_4 .

3.2. Various Conditions to Induce Superconductivity- High Pressure, Electrostatic Gating, Interface Engineering.

In the past several decades, various high-pressure techniques, including the BeCu clamp cell, the Bridgman cell and the diamond anvil cell (DAC), have been developed to create much higher pressures to push the limits of static pressure generation up to a few hundred GPa²⁴¹. High pressure techniques have been extensively used nowadays to explore the physical states of solids, to create new ground states in solids, to test theoretical models and help develop new theories.²⁴² Different from chemical doping route, high pressure is a clean tool to tune the interatomic distances, carrier concentration, effective electron-phonon interaction, Fermi surface topology, and magnetic order or spin fluctuations in solids without generating structural disorder or defects through chemical doping. The application of external pressure can drive intermetallic compounds towards or away from lattice instabilities by varying the principal parameters determining the superconducting properties such as the electronic density of states at the Fermi energy, $N(E_F)$, the characteristic phonon frequency, and the coupling constant of electrons and phonons, and it can

be used to tune the T_c and the superconducting properties. Very often, at high enough pressure, materials likely become unstable and undergo phase transformations into different structures of higher density and, frequently, of higher symmetry. Many of these new structures are metallic and superconductivity is observed in many high-pressure phases even when the compound was not superconducting at ambient pressure. For example, many of the naturally non-superconducting elements now have been turned into superconductors through the application of pressure, including non-metallic elements like sulfur²⁴³, iodine²⁴⁴ and rare-earth element europium²⁴⁵.

High pressure studies of superconductors could also provide additional insight to look for new superconductors. Soon after the discovery of the La-Ba-Cu-O (LBCO) cuprate superconductor in 1986³⁹, it was high pressure experiments (large positive pressure coefficient of T_c and the missing signs of saturation of T_c under high pressure) on this compound that demonstrated that a superconducting transition temperature (T_c) could be achieved above 50 K¹⁸¹ and suggested that the cuprate system warranted further exploration for novel physics. This led to the next important step in the search for new superconducting compounds that eventually raised the transition temperature above the temperature of liquid nitrogen. The T_c record for cuprates, at 164 K, was achieved in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9+\delta}$ (Hg1223) under high pressure ~ 30 GPa.⁶⁴

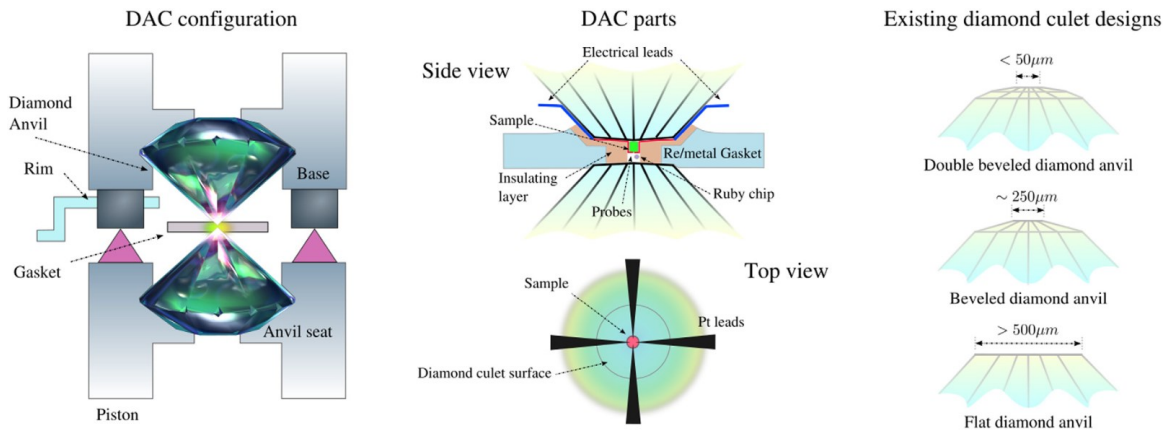


Figure 17. (Left) DAC schematic including anvil seats, gasket and pistons. **(Center)** detailed design of a DAC for transport measurements under pressure. **(Right)** different types of diamond

culets used in high-pressure experiments. Reprinted with permission from Ref. 246. Copyright [2020] [Elsevier B.V.].

The picture of DAC is shown in Figure 17.²⁴⁶ Two diamonds with culet sizes ranging from 50 microns to 500 microns are facing to each other separated by a Re gasket. The sample is placed in the gasket hole filled with a pressure-transmitting medium (inert gas, liquid or salts). In order to read the immediate pressure of the samples, one or more rubies will be placed into the gasket hole. Rubies will be kept away from each other as far as possible to ensure accurate pressure readings through fluorescence.

Some recent exciting results further support the concept that high-pressure techniques can provide enormous help on increasing the T_c or inducing the stability of superconductivity, with an eye towards future efforts in searching for room-temperature superconductors. In 2015, Drozdov et al. observed superconductivity in hydrogen sulfide, which was then proposed to be H_3S , at temperatures as high as $T_c = 203$ K at a pressure of 155 GPa.²⁴⁷ The high critical temperature is only 90 degrees away from room temperature and held the T_c record at that time. Four years later, Drozdov et al.²⁴⁸ and Somayazulu et al.²⁴⁹, independently set a new record for T_c by pressurizing in-situ-prepared LaH_{10} to 200 GPa - observing the existence of superconductivity up to 260 K which is only ~ -13 °C, below the annual average temperature of Antarctica. Although calculations and some experimental results have suggested a BCS-type mechanism for these materials, these pressure-induced high- T_c superconductors indeed pave the way for further exploration for more new high T_c superconductors and possibly room-temperature superconductors without using such high pressure in the future.

The electrostatic gating technique is another great technique to allow for the alteration and reversible change of the carrier concentration in materials, while, in principle, not changing the

level of disorder in the material.²⁵⁰ This technique is based on field effect transistor (FET) principles, to induce changes over a very wide range of carrier concentrations through a gating voltage to achieve substantial modifications of electronic and magnetic properties. As such, it could facilitate the controllable manipulation of various collectively ordered electronic phases and may lead to new states of matter/device development in a manner simpler than the approaches of chemical doping or high pressure. This technique in recent years has had a prevailing advantage to investigate the exotic superconductivity and their associated electronic structures in thin films or flakes at the atomic layer limit. A small amount of chemical doping and physical pressure would drastically change a materials morphology. From a practical standpoint, it was proven to be very hard to control the uniformity of electronic states in the material.

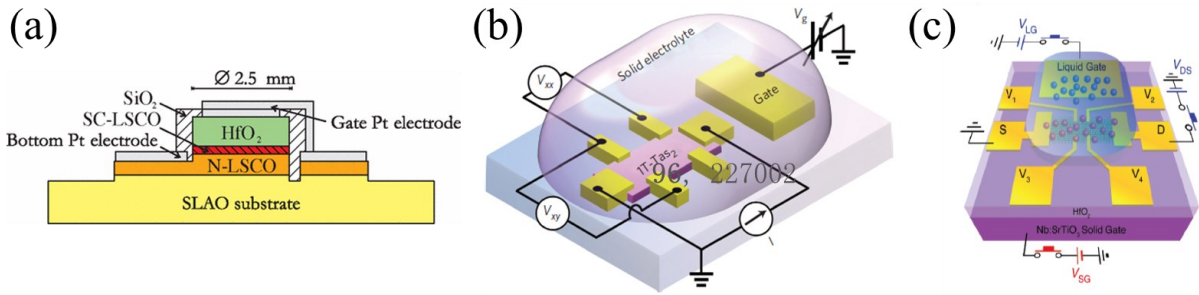


Figure 18. Schematics of three different device structure and measurement setups used for electrostatic gating: **(a)** a multilayer field effect transistor device; Reprinted with permission from Ref. 251. Copyright [2006] [American Physical Society]. **(b)** electro-chemical gating using a solid electrolyte; Reprinted with permission from Ref. 252. Copyright [2015] [American Chemical Society]. **(c)** electro-chemical gating using ionic liquids double layer transistors. Reprinted with permission from Ref. 253. Copyright [2012] [American Chemical Society].

We can classify this electric-field-driven doping technique into either electro-physical gating or electro-chemical gating, depending on the nature of the electrolyte used, as schematically shown in Figure 18. The electro-physical gating method uses conventional FET-like structures (Figure 18(a)) using an electrolyte without ions and insulating gate dielectrics.²⁵¹ The process

involves only electrons within the interface of the sample and electrolyte and the effect on the sample typically ceases when the voltage is removed. Electro-chemical doping uses an electrolyte ionic conductor such as a Li-ion electrolyte (Figure 18(b)) or an ionic liquid (Figure 18(c)) where ions can move into or out of the sample depending on the polarity of the voltage applied.^{252,253} In this case, the ions may stay in the sample even when the applied voltage is removed. It is an interfacial phenomenon in that electrostatic screening lengths can be on the order of a lattice constant, resulting in the induced charge being confined to within a few unit cells of the interface. This method has produced relatively high carrier densities (especially for the electro-chemical gating technique) that span the superconducting dome, and the entire phase diagram of a compound can be traversed by changing the gate voltage. Both gating techniques have been used to induce or modify superconductivity in variety of materials system such as cuprates^{251–254}, iron-based superconductors^{255,256}, ZrNCl^{257,258}, transition metal dichalcogenides^{259–263}, and twisted bilayer graphene^{264–266}.

Interface engineering provides another platform to study superconductivity. In this case, superconductivity emerges from interactions between deliberately engineered interfaces or hybrid systems^{267–271}. These interfaces could occur between chemically similar, isostructural materials (e.g., oxide-oxide, semiconductor-semiconductor), or dramatically dissimilar materials with different chemical bonding, crystal symmetries and electronic structures (e.g FeSe on SrTiO₃). The emergence of superconductivity or T_c enhancement in this case may be achieved by manipulating electronic and phonon surface states, the density of charge carriers, screening, the effective pairing interaction etc. Theoretically, the interfacial mechanism has been predicted to generate very high T_c , with the most theoretical pioneer work done by Little,⁶⁹ Ginzburg,²⁷² and Allender, Bray, and Bardeen (ABB).²⁷³

However, the requirements for such effective interfaces between different materials are rather stringent, e.g. perfect interface, intimate contact between the two materials, and the electrons near the interface can fill into the surface bands. Therefore, it typically requires advanced vapor deposition techniques, such as molecular beam epitaxy, to allow the requisite control of materials with atomically flat surfaces and interfaces. There is a wide range of tuning parameters available for interface engineering, including local chemical composition and structure, hybridization and proximitization between materials, control of strain, quantum confinement effects, including formation of two-dimensional electron gases, interfacial charge transfer, and electron-phonon or electron-magnon coupling, which can give rise to a wide range of novel phenomena as well.

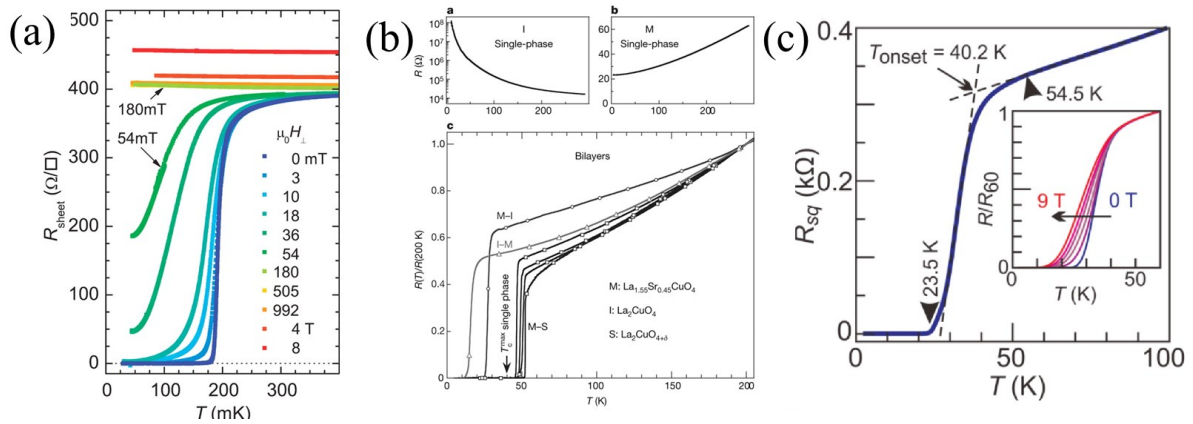


Figure 19. Three representative superconductivity originating from interface engineering: **(a)** Transport measurements on $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures extracted from Ref. 274. ²⁷⁴. Reprinted with permission from Ref. 274. Copyright [2007] [The American Association for the Advancement of Science]. **(b)** transport measurements on the $\text{La}_{1.55}\text{Sr}_{0.45}\text{CuO}_4/\text{La}_2\text{CuO}_{4+\delta}$ (M-S), $\text{La}_{1.55}\text{Sr}_{0.45}\text{CuO}_4/\text{La}_2\text{CuO}_4$ (M-I) and $\text{La}_2\text{CuO}_4/\text{La}_{1.55}\text{Sr}_{0.45}\text{CuO}_4$ (I-M) bilayer structures from Ref. 267. ²⁶⁷ (Reprinted with permission from Ref. 267. Copyright [2007] [The American Association for the Advancement of Science]) and **(c)** transport measurements of monolayer FeSe film on the Nb-doped SrTiO_3 substrate. Reprinted with permission from Ref. 282. Copyright [2016] [IOP Publishing].

The success of achieving interface superconductivity has been demonstrated in various hybrid material systems such as superlattices of chalcogenide semiconductors PbTe/YbS ,²⁷⁵

semiconducting oxides $\text{SrTiO}_3/\text{LaTiO}_3$ ^{276–278}, cuprate $(\text{La,Sr})_2\text{CuO}_4$ -based metal/superconductor bilayers,^{276,279,280} and monolayer $\text{FeSe}/\text{SrTiO}_3$ system,^{111,281,282} as shown in Fig. 19(c). The unusual high T_c , up to 65K, determined by spectroscopy studies in the $\text{FeSe}/\text{SrTiO}_3$ system is rather intriguing, as the reported T_c is much higher than that of pristine FeSe under strain with T_c at 37K.²⁸³ The complete understanding of interface superconductivity (e.g. why superconductivity only arises in certain interfaces not in others) and their microscopic mechanism may be beneficial if applied to the design of new materials that may lead to higher T_c in artificially made or naturally assembled material systems.

It is also proposed that the interface mechanism might occur naturally in some bulk grown crystals. For instance, Josephson tunneling has been reported in BSCCO single crystals along the c-axis,²⁸⁴ consistent with the metal/semiconductor model for interface superconductivity. Interface-enhanced superconductivity is also proposed recently to be responsible for the T_c enhancement observed in the rare earth doped CaFe_2As_2 ²⁸⁵ and undoped CaFe_2As_2 systems²⁸⁶.

3.3. Theoretical Predication and Machine Learning in Superconductivity.

Theoretical calculation, especially band structure theory, can aid in interpreting the electronic behavior of superconductors. Unlike molecular orbital theory in chemistry which depicts what real-space chemical bonds look like, band theory describes the electron's behavior in the reciprocal lattice of a solid by utilizing the wavevector dependence of the electron energies to generate an electronic structure. Moreover, the number of electrons in a solid material is huge - instead of forming discrete energy levels as for a single electron, the band structure gives a continuous energy range referred as energy band. One significant concept in band structure is the Fermi level/Fermi energy (E_F) which is defined as the highest energy level that electrons can

occupy at absolute zero in their ground states; that is, without further excitations, no electrons can occupy the energy bands beyond the Fermi level at absolute zero Kelvin. By presenting the calculation results of proposed material CaPt_5P , isostructural with reported MgPt_5P , in an electronic band structure figure, as can be seen in Figure 20(a), the possible states that electrons may occupy in a solid material may be estimated. Generally, E_F is set to be the zero-energy level in band structure figures. Despite the fact that there are many energy bands in the high-/low-energy regions, what impacts the physical properties of a compound are the energy bands near E_F . The density of states (DOS) reflects the number of electronic states per unit volume or per unit energy for certain energy level E , as shown in Figure 20(b). It is strongly correlated with band structure. With appropriate physical property measurements, one can intuitively interpret how the electrons' density of available states affect the properties.

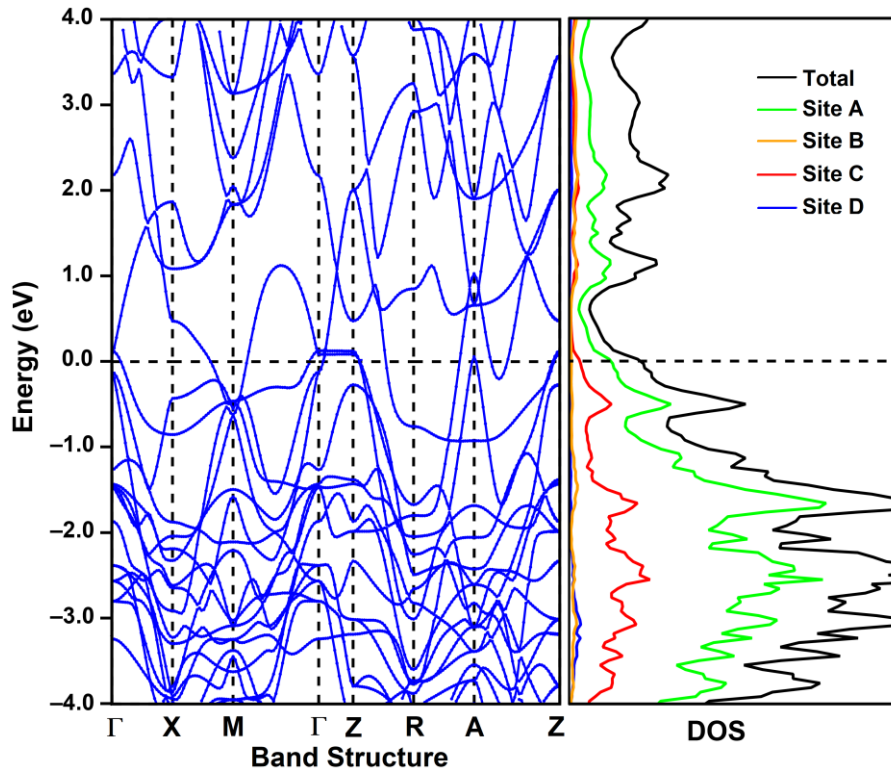


Figure 20. (Left) Band structure and (Right) density of states (DOS) of a proposed quaternary solid-state material with tetragonal unit cell and four atomic sites.

Extensive databases covering various superconducting materials properties allow a different “theoretical” approach, statistical and machine learning (ML) methods, to find new superconductors and optimize the critical temperatures (T_c) of superconducting materials. Such algorithms can be developed (trained) based on the variables from these superconducting databases, and employed to predict macroscopic properties, such as the critical transition temperatures in superconductors. Recently, scientists developed several different ML methods modeling T_c from the superconducting materials database.^{287–289} However, due to the lack of information of the direct factors that can influence the critical transition temperatures, such as lattice parameters, and band gaps it is hard for the current models to extract useful information for predicting the superconducting materials easily and straightforwardly.

4. Three Basic yet Important Characterizations needed When Reporting New Superconductors

Superconductivity is a macroscopic quantum state phenomenon, and many characteristic properties change drastically when superconducting compounds are cooled below the critical temperature T_c . Various advanced techniques and tools were developed in the past to study different aspects of the superconductors and unveil the exotic normal state and superconducting state of superconducting materials. However, whenever a new superconductor is reported, especially in bulk materials, there are three basic, yet important property characterizations needed to support the claim: zero electrical resistance, perfect diamagnetism, and a heat capacity jump. As there are very often many reports on preprint servers claiming the “discovery of room temperature superconductors” nowadays, these three simple criteria could also serve as the baseline for people to justify such claims to the research community.

The zero resistivity is the sudden transition from a state with finite electrical resistivity ρ above the critical temperature to a state with zero electrical resistivity below that temperature. This is the most direct and convenient way to identify superconducting components even in an inhomogeneous bulk material. This method is also quite sensitive, and typically a few percent of a superconducting component in a sample is already enough to cause a substantial resistivity drop. The T_c values determined from resistivity measurement are somewhat higher than those from thermodynamic measurements, as a tiny part of the materials becoming superconducting will lose its resistance, but a full resistance drop only realized if one or more full superconducting paths are in place between the electrodes. Therefore, various ways of defining superconducting T_c exist in the literature with onset, 10%, 50%, 90% or full resistivity drop points noted. One needs to be careful when comparing the results based on different criteria. The sharpness and superconducting

transition width from the normal state to full resistivity drop, could be used as a measure of the homogeneity or purity of the superconducting sample. For instance, the 90%-10% resistivity superconducting transition width for pure lead with T_c of 7.2K can be less than 0.01K, yet highly impure lead can have a much wider transition. Polycrystalline samples should be pressed into dense pellets for these measurements, and often thermally annealed before conducting electrical resistivity measurements in order to reduce the voids and minimize grain boundary contact resistance. Sometimes, single crystal and thin films are not quite adhesive to the conventional electrical contact used, and sputtered metal contacts will be needed to have good contacts before measurements. One has to bear in mind that resistivity is a transport, but not a thermodynamic quantity and is strongly affected by grain boundaries in the measurement samples. Filamentary paths (impurity phase, inhomogeneous sample) may result in sharp drops of resistivity or even zero ρ , but this does not necessarily represent the intrinsic nature of the samples.

The second hallmark for superconductors is the Meissner effect, discovered by German physicists Walther Meissner and Robert Ochsenfeld in 1933.²⁹⁰ It describes the expulsion of magnetic flux from inside superconductors when they are cooled down below T_c and thus results in diamagnetic state. The degree of diamagnetic state of superconductors is characterized by volumetric magnetic susceptibility (sometimes called volume fraction), $4\pi\chi_v$ where χ_v is defined as $(M/H)/V$ (M = magnetic moment; H = applied magnetic field in Oe; V = volume of material). It reveals bulk superconductivity while $4\pi\chi_v = -1$. The difference between normal diamagnetism and diamagnetism due to the Meissner effect is that the former originates from the spin of electrons in matter, but the later is induced by the currents flowing to screen the applied magnetic field, and is much larger than standard diamagnetism. Superconductors can be classified into two distinct types based on their response to an external magnetic field. In type I superconductors, perfect

diamagnetism with $4\pi\chi_v = -1$ continues until the critical magnetic field H_c is reached, at which point the perfect diamagnetism is suddenly destroyed, while in type-II superconductors, two different critical fields can be identified with lower critical field (H_{c1}) and higher critical field (H_{c2}). In the region below H_{c1} , the material behaves the same as a type I superconductor. In between H_{c1} and H_{c2} there exist non-superconducting regions where the magnetic field can penetrate with “vortices” of shielding current around those small regions, leading to mixed superconducting/non-superconducting states. The magnetization of type II superconductors often exhibits hysteresis, i.e it depends on the previous history of how the external magnetic field was applied. Therefore, proper magnet demagnetization and reset is typically recommended if a higher field than 1T is used prior to the magnetic susceptibility measurement of new superconductors. There are two aspects to perfect diamagnetism in practical measurements. The first is flux exclusion, where the material in normal state is zero-field-cooled (ZFC) below T_c without magnetic field; the second is flux expulsion, where the material is field-cooled (FC) below the T_c in the presence of magnetic field. For defect-free high-quality spherical samples, one would expect the ZFC and FC susceptibilities to be nearly identical. As most new superconductors are not perfect, the existence of impurities and holes can serve as strong pinning centers, which impede the expulsion of magnetic flux from the sample if it has penetrated, this thus strongly affects the measurements and causes bifurcation of the ZFC and FC susceptibility curves. In addition, the shape of the sample can have a significant effect on the induced shielding current and thus affect the measured ZFC susceptibility value, especially for layered materials with large anisotropy. Sometimes, one will observe a volumetric magnetic susceptibility beyond -1 during the ZFC measurement. Under that situation, it is necessary to make a demagnetization field correction to determine the exact internal field in the solid and subsequently the measured susceptibility values. In general, after

demagnetization factor correction, one can consider the “shielding fraction” based on ZFC susceptibility as the upper limit of the true superconducting fraction of the measured samples, and the volume fraction based on FC susceptibility generally represents the lower limits of the true superconducting fraction of the measured sample, and it’s best not to use it to determine the amount of superconducting material present.

The third basic measurement of superconductors is the specific heat measurement. This is a thermodynamic quality truly representing a “bulk” measurement of the entire sample, which should not be overlooked when reporting new superconductors, especially when one or more of the constituted elements or impurities are superconducting. A recent report by Carnicom et al.,²⁹¹ is highly recommended as tutorial material to emphasize such importance. The superconducting transition in the absence of magnetic field is a second-order phase transition, this will cause a discontinuity in the specific heat. The BCS theory, in which electrons form Cooper pairs through the electron-phonon interaction, predicts that the electronic specific heat jumps abruptly at T_c with $\Delta C_e/\gamma T_c = 1.43$. The electronic specific heat could be obtained through subtracting the normal state specific heat from the zero-field superconducting specific heat data. The normal state specific heat typically follows the Debye model $C = \gamma T + \beta T^3$ (sometimes a T^{-2} term is added to consider the Schottky contribution). Through fitting, one can obtain the Sommerfeld coefficient γ , which is proportional to the electronic density of states (DOS) at the Fermi level, and the β value, which is directly related to Debye temperature through relationship $\Theta_D = (12\pi^4 \kappa_B N_A Z / 5\beta)^{1/3}$. The subtracted electronic specific heat will depend exponentially on temperature following the BCS prediction in the temperature range below T_c with a relationship $C_e \sim \exp(-\Delta/\kappa_B T)$ where the Δ superconducting gap defined by BCS and 2Δ corresponds to the minimum energy needed to break a cooper pair and create an electron-hole pair quasiparticle excitation. This temperature dependent electronic

specific heat, and $\Delta C_e/\gamma T_c = 1.43$ discontinuity at T_c are typically used to verify whether the new superconductors fall into the conventional BCS picture. For conventional superconductors with stronger or weaker-coupling than the BCS weak-coupling value, an semi-empirical α -model, is often used to find the size of the gap, where $\alpha = \Delta/\kappa_B T_c$ is a free parameter rather than fixing α at the BCS value of 1.764. For unconventional superconductors, on the other hand, their specific heat won't necessarily follow the BCS prediction, and various unusual scalings of T_c and γ have been discussed. The electronic contribution coefficient γ can vary a lot for different types of superconductors. Normally, γ is a relatively small value, ~ 10 mJ/mol/K² or less for most BCS superconductors and some unconventional superconductors such as BKBO and BSCCO. These values are expected as γ is proportional to the effective mass m^* of the conduction electrons. However, in some cases, strong correlations between localized f -electrons (i.e. for rare earth elements or actinides) and conduction electrons will cause renormalization of the quasiparticles effective mass m^* , which may exceed the ordinary effective mass by several orders of magnitude (i.e heavy fermions). As a result, a much higher γ value will be obtained when $T \rightarrow 0$ for heavy fermion superconductors. It is also worthwhile to note, in ordinary cases, that the residual γ value in the superconducting state (often called γ_0) can provide some additional information regarding to the sample quality. When part of the sample remains normal due to impurities or defects, one can expect a higher value of γ_0 than that from a high-quality counterpart sample. Therefore, this parameter could be used to provide additional information regarding to the “true” superconducting fraction in the measured samples as well.

5. Perspectives for Future Study from Chemistry and Physics Perspectives

5.1. Exploring New Superconductors.

Although the theory of phonon-mediated superconductors and some modified superconductivity mechanisms have been established for many years, the prediction of novel superconductors remains a difficult and long-standing goal for solid-state chemists, condensed matter physicists and material scientists. It is extremely difficult to incorporate every feature of all superconductors together and propose a universal “superconducting designing strategy”; thus most design strategies for novel superconductors are empirical. Herein, we will try to integrate them with chemical perspectives and provide a basic idea, based on inducing superconductivity from unstable electronic structures. We can approximately consider superconductivity as being similar to other physical phenomena, such as charge-density-waves (CDWs), spin-density-waves (SDWs) and magnetism. Electrons in superconductors form Cooper pairs to balance unstable electronic structures. Thus, we can understand:

1. Doping electrons or holes into insulators or semiconductors to induce superconductivity. The most famous examples are the two prominent families of high- T_c superconductors, cuprates and iron-based superconductors, which can be approximately considered as resulting from doping insulators/semimetal to induce superconductivity.

2. Suppressing other physical phenomena such as CDWs, SDWs to induce superconductivity. It is well-known that CDWs can compete, coexist or cooperate with superconductivity somehow in low-dimensional systems (layered compounds). Even though the relationship between CDWs and superconductivity is still under debate, people still made some progresses onto inducing or enhancing superconductivity by suppressing CDWs. For example, 1T-TaS₂ shows multiple CDWs at different temperatures.^{292,293} By doping onto the S site,

superconductivity can be induced and coexists with the CDW state. Another example is that high- T_c superconductivity can be induced by suppressing the charge disproportion on the Bi site in BaBiO_3 .³⁷

3. Applying high pressure to induce superconductivity. As described above, superconductivity can be induced or enhanced by applying pressure, for example, the previously mentioned LaH_{10} and H_3S .^{247–249} Another famous high-pressure superconductor is BaFe_2As_2 , the parent compound of 122-type Fe-based superconductors.¹⁰⁶ While applying pressure of 4 GPa, superconductivity can be induced in layered BaFe_2As_2 single crystals below $T_c = 29$ K. Besides applying physical pressure, where the diamond anvil cell is used to adjust pressure, tuning chemical pressure is another successful way to induce or enhance superconductivity.

4. Using the valence electron counting method to find new superconductors. This is a useful chemical and empirical method when designing new superconductors, proposed by Matthias. He summarized the “valence-electron concentration (VEC)-dependence of superconducting transition temperature” for the compounds he investigated and found that in order to get a high- T_c superconductor, one needs to ensure that the number of valence electrons per atom should be around either 5 or 7 valence electrons/atom. Similar result was concluded in the review written by Arndt Simon who indicates two optimal values of 4.75 and 6.5 valence electrons per atom.

5. Proposing new critical charge transfer pairs for superconductors. “Critical pairs” of atoms in the periodic table can be postulated as having the delicate charge-transfer balance between covalent and ionic bonding. Critical charge-transfer pairs in superconductors can be considered as a critical way for a compound to respond to perturbations and can lead to superconductivity. Because superconductivity can be induced by introducing perturbation into a stable system, as what we discussed in section 3.1, by forming or breaking specific chemical bonding with critical

charge-transfer pairs. More interestingly, the charge-transfer pairs usually occur in individual layers, i.e., the active block in cuprate superconductors and Fe-As in IBSCs. Recently, we proposed Ru-Sb as the new critical charge transfer pair that is critical to the superconductivity in $\text{Hf}_5\text{Sb}_{3-x}\text{Ru}_x$.

In the past 30 years, the community never gave up looking for other high- T_c superconductors. One key strategy is to search for nickelate superconductors. Numerous studies have been done to search for high T_c superconductors among bulk nickelates. In 2019, after many years of searching, the Hwang group reported superconductivity in Sr-doped NdNiO_2 thin films, with $T_c \sim 9\text{-}15\text{ K}$.²⁹⁴ Thus the interest in nickelate superconductors has been ignited again.

5.2. Microscopic Unified Theory for Unconventional Superconductors including the Pairing mechanism

The search for novel superconductors is intricately connected to our ability to elucidate, model, and predict the electronic properties of materials. Therefore, the development of theoretical tools to achieve a complete quantitative and unified understanding of phenomena and exotic properties of existing superconductors and meanwhile provide guidance to look for new superconductors will be important. Clearly, we need to pay attention to all novel superconductors, regardless of their transition temperature and pairing mechanism. Some of the materials might have low transition temperature, such as heavy fermion or organic superconductors, but the theoretical understanding of these superconductors might have broad impact and open doors towards an ultimate unified theory.

The Bardeen-Cooper-Schrieffer (BCS) theory, initialized in the 1950s and further developed by many theorists, is extremely robust and provides clear descriptive power to understand most of the conventional superconductors. The fundamental picture of the BCS theory

as developed is that the electron-phonon interaction induces a superconducting state by pairing up electrons with the opposite spins and crystal momenta. The Cooper pair, as part of a highly correlated state, is free to move through the lattice, in contrast to a localized electron pair. However, the BCS theory cannot provide a definite and predictive guide in searching for new superconductors, especially for new superconductors incorporated with spin or valence fluctuations. Although recent theoretical calculations based on BCS theory using modern density-functional theory (DFT) codes have been quite successful in explaining the crystal structures and their associated high T_c in H-rich H_3S and LaH_{10} at high pressures the theory did not predict that these compounds in specific should be superconducting, only that “lightweight atoms give high phonon frequencies and therefore should yield high T ’s.” These results are rather encouraging, though, as the superconductivity in these materials appears to be based on well-understood BCS theory - by taking advantage of the high Debye temperature and strong electron-phonon coupling in these H-derived materials. It also provides the hope that some appropriate chemical and structural modified phases, which mimic the effect of pressure, could be realized at ambient pressure in the future with similar or even higher T_c .

A unified theoretical understanding of unconventional superconductors, especially in strongly correlated systems such as heavy fermion, cuprates and iron-based superconductors, is even more challenging. It requires a much better understanding of the underlying multiple interactions in a compound, and maybe some model including more than one pairing mechanism to adequately account for the variety of existing experimental data. For examples, in the two large classes of high T_c superconductors, cuprates and iron-based superconductors, different pairing symmetry and different yet quite complex phase diagrams have been discovered experimentally. Multiple forms of electronic ordering appear to be spatially coexisting with superconductivity,

such as the pseudogap in cuprates and electronic nematic phases in the Fe-based superconductors. The physical origins of these magnetic, orbital, and charge ordered states in the materials, and their role in the superconducting pairing interaction (i.e. a consequence of a cooperative, intertwined, or competing interaction) in different materials needs to be theoretically and experimentally well understood. A new paradigm by combination of novel theoretical approaches and more powerful computational tools needs to be developed and implemented to unveil the principles that govern the different strengths of these ordered states (e.g. spin, orbital and charge), their interactions, and control and optimization these interactions to design and discover new superconductors with desired electronic and superconducting properties. If this could ever be realized or even partially understood, it could provide certain knowledge to experimentalist to tune and optimize materials in their experimental trials, and eventually enhance our ability to search for new superconducting materials.

Last but not least, developing theoretical and computational algorithms and models to describe the processes that occur at the contacts and interfaces between superconductors and normal metals, including nanoscale superconductivity, possible various exchange interactions and electrical transport across the interfaces, as exemplified in the interface enhanced superconductivity observed in monolayer FeSe/SrTiO₃ thin films, is important. The conventional superconductor can be considered as an entangled state, involving a superposition of different numbers of Cooper pairs. Integrating the superconductivity with other quantum phenomena, especially topological quantum states, is of great interest because such materials may host Majorana fermions (MF, neutral charge fermions) as protected boundary modes and are hence relevant for quantum computing. Current research has been focused on hybrid structures via the superconducting proximity effect, which involve an *s*-wave (conventional) superconductor, an

external magnetic field, and certain non-SC materials. However, synthesis of hybrid structures highly depends on epitaxial relationships and growth kinetics; only limited materials can be grown in this way. Thus, investigating topological superconductors in naturally occurring superconductors attracts lots of attention. Even though many bulk superconductors have been discovered in past decades, to date, only a handful has been explored in depth as candidates for topological superconductivity, such as Sr_2RuO_4 which displays proposed chiral $p + ip$ superconductivity occurring at ~ 1 K.^{295–296} Exploring new routes to topological superconductors in bulk materials by design, and to synthesize and characterize novel misfit phases with the coexistence of superconducting and topological fragments is highly demanding for realizing Majorana fermions that particles are their own antiparticles.

6. Conclusion

This comprehensive review focuses on some existing well-known superconductors, i.e., A15 superconductors, Chevrel phases, heavy-Fermion superconductors, cuprate superconductors, bismuthate superconductors, iron-based superconductors, high-pressure superconductors and interface superconductivity. A brief introduction about how to characterize superconductors is presented. It is already more than 100 years from the first discovery of superconducting mercury, with the superconducting critical temperature enhanced from 4.2 K to 135 K under ambient pressure. Even though with high pressure T_c can be increased to ~ 250 K, the application of superconductors in common systems seems still unapproachable. However, we are confident that by comparing crystal structures, electronic structures and physical properties of different types of superconductors, ambient-pressure room-temperature superconductors will someday be obtained.

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9. Biographies

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