

## Chapter 2

# Overview of Superconducting Materials with $T_c$ Higher than 23 K

**Abstract** Among the eight families of high- $T_c$  superconductors, magnesium diboride ( $\text{MgB}_2$ ), borocarbide ( $\text{YPd}_2\text{B}_2\text{C}$ ), and calcium (Ca) at high pressures are thought to be conventional superconductors with phonon-mediated pairing.  $T_c = 39$  K for a simple metal  $\text{MgB}_2$  is surprising in view of the old-known ceiling of 30 K of the electron-phonon mechanism. Several circumstances in  $\text{MgB}_2$  appear to optimize the phonon-mediated pairing and to up-shift the old ceiling of  $T_c$ . These give a hint on further optimization or further enhancement of  $T_c$ . In doped bismuthates ( $\text{BaBiO}_3$ ), fullerenes ( $\text{C}_{60}$ ), and chloronitrides ( $\text{HfNCl}$ ), dominant pairing interaction is also supposed to be electron-phonon coupling. These superconductors are proximate to insulating phases. Because of this, the electron (carrier) density is significantly low as compared to that in simple metals, suggestive of contribution from electron-electron interactions which may act to strengthen electron-phonon coupling. One other family, from organic compounds, is going to join the latter group. Copper oxides and iron arsenides/selenides, as well as heavy fermions compounds, are distinct from others, and obviously belong to unconventional superconductors with dominant electron-electron interactions.

## 2.1 Introduction

Among the eight families of high- $T_c$  superconductors (HTSCs), superconductivity in  $\text{PdY}_2\text{B}_2\text{C}$ ,  $\text{MgB}_2$ , and elemental Ca in the high-pressure phase is discussed in the context of superconductivity with the phonon-mediated pairing interaction. Superconductivity in  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  (BKBO), doped  $\text{C}_{60}$  and  $\beta\text{-HfNCl}$  are also supposed to be phonon-mediated, but the estimated  $T_c$  values are significantly lower than those of real materials. As these three are in proximity to some insulating phases, it is plausible that contributions from electron-electron interactions (electronic correlations) enhance the electron-phonon coupling. A possible high- $T_c$  organic superconductor, doped polycyclic-aromatic-hydrocarbon, might join the second group. All these families, except Ca, have light elements, B, C, N, or O and strong covalent bonds, so that large energy prefactor  $\Omega_\theta$  (phonon frequency) and strong electron-phonon coupling  $\lambda$  in a simplified formula,  $k_B T_c \sim \hbar \Omega_\theta e^{-1/\lambda}$ , are presumably important factors for high  $T_c$ 's.

Although there is uncertainty in evaluating the parameter for screened/renormalized Coulomb interaction, usually parameterized by  $\mu^*$ , the calculation of  $T_c$  in the framework of the Migdal-Eliashberg theory successfully reproduces  $T_c = 39$  K of  $\text{MgB}_2$ , the highest  $T_c$  so far achieved in obviously weakly correlated systems.  $T_c = 39$  K for a simple metal  $\text{MgB}_2$  is surprising in view of the old-known ceiling of 30 K of the electron-phonon mechanism. Several circumstances appear to be optimized in  $\text{MgB}_2$  to allow for very strong electron-phonon coupling without inducing lattice instability.

Copper oxides and iron arsenides/selenides, as well as  $\text{PuCoGa}_5$  with  $T_c = 18$  K derived from heavy fermions compounds, are distinct from others, and obviously belong to unconventional superconductors with dominant electronic correlations.

## 2.2 Materials with Phonon-Mediated Pairing

For superconductors with phonons as pairing glue,  $T_c$  is understood or the  $T_c$  value is calculated in the well-established framework of the Migdal-Eliashberg theory. Two important parameters that determine  $T_c$  are the electron-phonon coupling strength  $\lambda$  and the phonon frequency  $\Omega_0$ . Large  $\Omega_0$  and strong  $\lambda$  are favorable for high  $T_c$ , while the phonon energy  $\hbar\Omega_0$  needs to be considerably smaller than the Fermi energy  $E_F$  of the electronic system,  $\hbar\Omega_0 \ll E_F$  (the Migdal (retardation) condition). The Migdal condition is necessary for the bare Coulomb repulsive interactions ( $\mu$ ) between electrons to be significantly renormalized (decreased);

$$\mu^* = \mu / [1 + \mu \ln (E_F / \hbar\Omega_0)].$$

The coupling strength  $\lambda$  is usually expressed by

$$\lambda = N(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle = N(E_F) V_{ph},$$

with  $\langle I^2 \rangle$  being the mean-square electron-phonon matrix element averaged over the Fermi surface,  $N(E_F)$  the electron density of states at the Fermi energy,  $M$  the ion mass,  $\langle \omega^2 \rangle$  the averaged square phonon frequency, and  $V_{ph}$ , the effective electron-phonon interaction. In a crude approximation, that is a guide for extracting important parameters for  $T_c$ ,  $\langle \omega^2 \rangle \sim K/M$  ( $K$ , stiffness of the lattice) and  $T_c$  is approximated by the McMillan formula,  $k_B T_c \sim \hbar\Omega_0 e^{-1/(\lambda - \mu^*)}$ . More rigorously,  $T_c$  is expressed by the McMillan-Allen-Dynes formula [1]. In the strong coupling limit (large  $\lambda$ ), the formula has an asymptotic form,  $T_c \sim \lambda^{1/2}$ , and  $T_c$  continues to increase, if other parameters are kept unchanged.

These equations suggest that larger  $N(E_F)$ ,  $\langle I^2 \rangle$ , and  $\Omega_0$  are favorable for higher  $T_c$  values. Some of the old Matthias rules, #1: cubic crystals #2:  $d$ -electron metals, and #3: special average number of valence electrons, are guides to a search for materials with larger  $N(E_F)$ . Also, metals composed of light elements (small  $M$ ) with stiff lattice (large  $K$ ), hence large  $\Omega_0$ , were candidates for high- $T_c$  SC. Since  $V_{ph}$  is

independent of  $M$  and  $\Omega_0 \sim 1/M^{1/2}$ , it was expected that materials composed of light elements would have a large  $\Omega_0$  and a substantial  $\lambda$ . Metallic hydrogen (H) was supposed to be the limiting case as predicted in 1968 [2], but realization of HTSC in metallic hydrogen remains challenging.

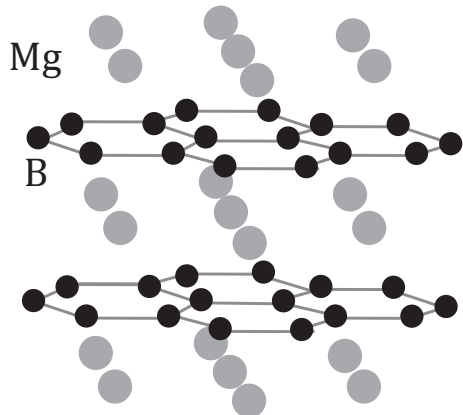
However, there were discussions on the  $T_c$  ceiling for SC with phonon mediated pairing:

1. The magnitude of  $T_c$  is bound by the inequalities,  $k_B T_c \ll \hbar \Omega_0 \ll E_F$ , so it was thought that  $T_c$  could not be high.
2. Large  $N(E_F)$  is a characteristic of narrow band metals which implies a small  $E_F$ . This tends to make the renormalization of repulsive interaction weaker. Materials with a pronounced peak in  $N(E)$  at  $E_F$  which was expected by the Matthias rule #3, have tendency for electronic and structural instabilities and their  $T_c$  would be sensitive to disorder or impurities.
3. The old idea, which is not necessarily correct, is that  $\Omega_0$  and  $\lambda$  are not independent parameter; when  $\Omega_0$  is large,  $\lambda$  cannot be large, since the formula for  $\lambda$  contains  $\Omega_0^2$  in its denominator.
4.  $T_c$  for SC in the strong coupling regime is thought to monotonically increase following the Allen-Dynes formula,  $T_c \sim \lambda^{1/2}$ . However, even so, too strong electron-phonon coupling induces a structural instability which gives a ceiling.

## 2.3 High- $T_c$ Superconductivity in $\text{MgB}_2$

In this regard,  $\text{MgB}_2$  with  $T_c = 39$  K is a surprising material [3]. As shown in Fig. 2.1, the crystal structure consists of a stack of hexagonal honeycomb Mg layer sandwiched by hexagonal B layers above and below. It is a sort of fully intercalated graphite structure. The B-B bond is a strong covalent bond arising from the  $sp^2$  hybridization, and hence the corresponding bond-stretching phonon modes have high frequencies ( $\Omega_0 \sim 1000 \text{ cm}^{-1}$ ) [4].  $\text{MgB}_2$  is obviously a simple metal in the normal

**Fig. 2.1** Crystal structure of  $\text{MgB}_2$



state and phonon-mediated SC is evidenced, for example, by the boron isotope effect (for  $^{10}\text{B} \rightarrow ^{11}\text{B}$  isotope substitution  $T_c$  decreases by 1 K [5]).  $\text{MgB}_2$  is basically a weakly correlated (*s*)*p*-band metal with large Fermi energy  $E_F \sim$  several eV which is much larger than the highest energy phonon ( $\sim 0.1$  eV), so that SC is understood within the framework of the Migdal-Eliashberg theory. Indeed, the calculation of  $T_c$  based on the density-functional theory (DFT) and linear-response theory (LRT) in the local-density approximation (LDA) successfully reproduces  $T_c = 40$  K [6], though the renormalized Coulomb repulsion  $\mu^*$  is adjusted to  $\mu^* = 0.09\text{--}0.13$  which are used for conventional superconductors.

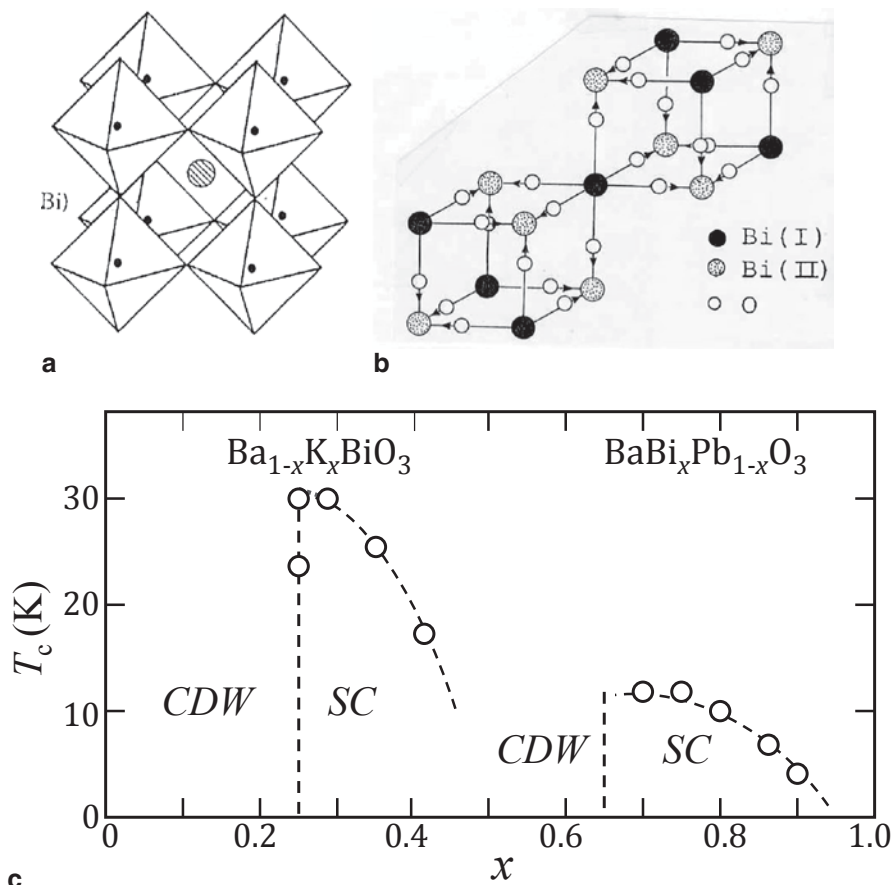
The crucial ingredients for the high- $T_c$  value in  $\text{MgB}_2$  are thought to be the followings:

1. Layer structure:  $N(E_F)$  maintains a substantial magnitude even when  $E_F$  is located near the band edge, since the electronic density of states is nearly constant against energy in two dimensions.
2. Strong  $sp^2$  bonding: Layer structure favors  $sp^2$  hybridization/bonding. The  $sp^2$  bond is much stronger than *d-d* bond, and even stronger than  $sp^3$ .
3. Light element B: Combined with the strong  $sp^2$  bond leads to very large  $\Omega_0$ .
4. Very strong electron-phonon coupling without instability: There is a cylindrical FS (so-called  $\sigma$ -FS) with character of strong bonding orbitals ( $E_F$  crosses the  $sp^2$  hybridized bands) which couples strongly to the B-B bond stretching phonon modes. The calculated deformation potential  $\Sigma_D$ , a change of electronic band energy due to lattice distortion by a unit length ( $\text{\AA}$ ) corresponding to a specific phonon mode, is  $\Sigma_D = 13 \text{ eV} / \text{\AA} (\langle I^2 \rangle \propto \Sigma_{D^2})$ . If the electronic system very strongly couples with a particular phonon mode at momentum  $Q$ , the frequency of this phonon is strongly renormalized and softened, and the lattice becomes unstable. In the case of  $\text{MgB}_2$  the relevant FS is circular associated with 2D parabolic bands, so there is no nesting Fermi surface nor a special  $Q$ . The electron-phonon coupling is very strong ( $\lambda \sim 0.82$ ) for phonons in the two bond-stretching branches. This gives rise to nearly constant  $\Omega$ -renormalization over a range of  $Q$ 's with  $\Omega$  remaining large, and thereby the material avoids a structural instability.
5. Band degeneracy  $n_B = 2$ :  $\text{MgB}_2$  is a multiband/multiple FS system. There are two almost identical but separated  $\sigma$ -FSs which are relevant to the strong coupling with phonons in the two bond-stretching mode branches exist in the 1st BZ. In this case  $\lambda$  is further enhanced by a factor of  $n_B^2 = 4$  [7]. These seem to conspire to optimize the phonon-mediated superconductivity in  $\text{MgB}_2$ .

## 2.4 Other Electron-Phonon Superconductors with Fairly High $T_c$

### 2.4.1 Doped Bismuthate $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  (BKBO) shows superconductivity at  $T_c \sim 30$  K [8, 9]. The parent compound  $\text{BaBiO}_3$  is a distorted perovskite oxide (see Fig. 2.2a), and a three-



**Fig. 2.2** **a** Idealized perovskite structure of  $\text{BaBiO}_3$ . Actual structure is distorted due to breathing-mode distortion and rigid rotation of  $\text{BiO}_6$  octahedra. **b** Breathing-mode distortions in the CDW state of  $\text{BaBiO}_3$  which make the compound insulating with inequivalent neighboring Bi atoms [10]. **c** Temperature ( $T$ )-doping ( $x$ ) phase diagram of doped  $\text{BaBiO}_3$ ,  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  and  $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_3$ . The superconducting region is bounded by a half-dome in both cases. Most of the remaining region is CDW state which is so robust that the CDW transition temperature is too high to be chased

dimensional charge-density-wave (CDW) insulator with a CDW gap of 2 eV [10]. CDW is supposedly an array of alternating  $\text{Bi}^{3+}$  ( $6s^2$ -lone pair) and  $\text{Bi}^{5+}$  (closed shell ion). In reality, only little charge difference on the Bi sites is observed, but the oxygen sites are distorted, the breathing-mode distortion—the O atoms expanding around a Bi atom and shrinking around the neighboring Bi atom as sketched in Fig. 2.2b. The CDW order is quite stable and never melts up to temperature 1000 K. It melts by substituting (doping) K for Ba ( $x \sim 0.3$ ) or Pb for Bi ( $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_3$ ,  $x \sim 0.6$ ), giving way to superconductivity. The phase diagram is displayed in

Fig. 2.2c. The CDW order occupies a wide region of the phase diagram and is quite stable. As a consequence of the robust CDW, strong CDW fluctuations either static or dynamical, remain viable even in the SC regime [11].

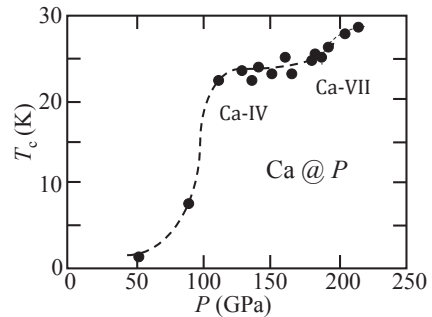
The electron-phonon coupling estimated by the DFT and LRT in the local-density approximation (LDA) is  $\lambda=0.34$  [12] which is well below the value required to account for SC with  $T_c \sim 30$  K. This failure indicates some correlations beyond LDA need to be incorporated, since the LDA tends to underestimate  $\lambda$  due to over-screening. This is particularly the case with materials in the vicinity of a metal-insulator transition. SC in the doped bismuthates is realized in the metallic side of the CDW insulator-metal transition and  $T_c$  is high in close vicinity of the transition. An attempt to go beyond LDA shows that  $\lambda$  is enhanced by a factor of 3 by taking into account of nonlocal electronic correlation effect arising from a poor screening [13]. The value of  $\mu^* \sim 0.1$  is estimated by first-principle calculations. Using the enhanced  $\lambda$ , the renormalized  $\Omega$ , and  $\mu^*$ ,  $T_c$  is calculated to be 30 K from the modified McMillan equation.

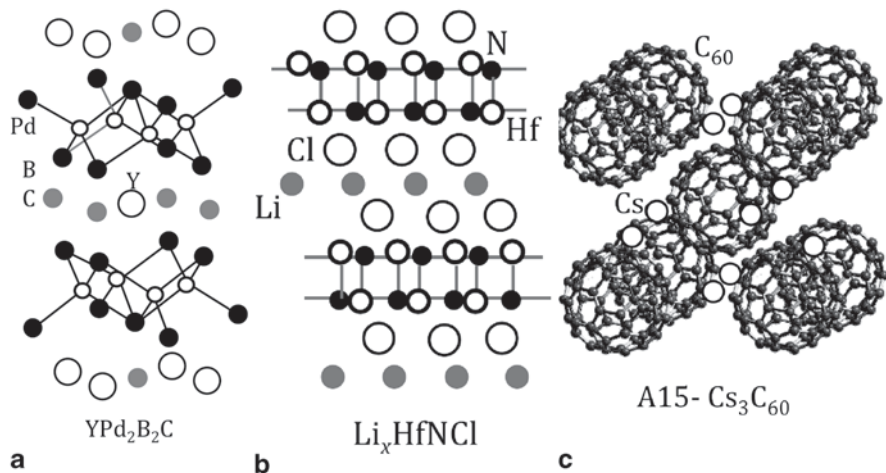
#### 2.4.2 Elemental Superconductors at High Pressures

In the last 15 years a number of elements have been found to be SC with fairly high  $T_c$  values under pressures ( $P$ ) of 30–50 GPa or higher. These include sulphur (S) ( $T_c = 17$  K) [14], lithium (Li) ( $T_c = 20$  K) [15], yttrium (Y) ( $T_c = 20$  K) [16], and calcium (Ca) ( $T_c = 29$  K) [17, 18]. As in the case of  $\text{MgB}_2$ , for these elemental SCs the LDA-based calculations appear to be successful in deriving large  $\lambda$  and estimating high  $T_c$ . Li is an  $s$ -electron metal and is not expected to have large electron-phonon coupling  $\lambda$  despite its light atomic mass. In fact,  $T_c$  of Li at ambient pressure is only 100  $\mu\text{K}$ . The enormous increase of  $T_c$  at high pressures is ascribed to the transformation from an  $s$ -band metal to an  $s$ - $p$  metal [7] in which the covalent character is possibly added to the bonding and thus Li may possess necessary ingredients for high  $T_c$  in common with  $\text{MgB}_2$ .

Ca in the high- $P$  phases have distinctly higher  $T_c$  and joins the group of HTS. As plotted in Fig. 2.3,  $T_c$  rapidly rises in the  $P$  range between 50 and 100 GPa, reaching

**Fig. 2.3**  $T_c$  of calcium plotted as a function of pressure (the data points are from [17, 18])





**Fig. 2.4** **a** Crystal structure of  $\text{YPd}_2\text{B}_2\text{C}$ . **b** Crystal structure of  $\beta\text{-HfNCl}$ . It becomes a superconductor at  $T_c = 26$  K upon electron doping. **c** A15 type crystal structure of  $\text{Cs}_3\text{C}_{60}$ .  $T_c = 38$  K is achieved upon applying pressure [29]

25 K at  $P = 160$  GPa in the Ca IV structural phase [17]. With further increase of  $P$ ,  $T_c$  gradually rises to 29 K at  $P = 220$  GPa [18] where Ca is in the distinct Ca VII phase with so-called “host-guest” structure [19]. It is surprising that Ca is not a light mass element. It is unlikely that Ca under pressure is a strongly correlated electronic system with some magnetic state nearby because of its proximity to the  $3d$  transition-metal elements. Instead, as the Ca IV and VII phases are structures with high-density of Ca atoms which is by a factor of 4–5 higher than that at ambient pressure, hardened phonons and/or a  $3d$  orbitals mixing may strengthen electronic correlations and enhance the electron-phonon coupling as in the case of the doped bismuthates.

### 2.4.3 Borocarbide $\text{YPd}_2\text{B}_2\text{C}$

Among the family of borocarbides,  $\text{YPd}_2\text{B}_2\text{C}$  has the highest  $T_c = 23$  K [20]. Since single crystals are not available, its physical properties and material parameters have not been studied yet. Instead, most extensively studied compounds are the Ni borocarbides, representatively  $\text{YNi}_2\text{B}_2\text{C}$  ( $T_c = 15$  K). The basic building block of the layer structure, displayed in Fig. 2.4a, is a B-C-B trimer (double dumbbell) linked to  $\text{YNi}_2$  layers. The Ni-B configuration is the same as that of Fe-As (Se) in the Fe-based high- $T_c$  superconductors (see Chap. 4). The strong B-C-B bonds and light masses give rise to high-frequency optical phonon modes ( $\sim 1000$   $\text{cm}^{-1}$ ) well separated from the low-lying phonons. The high-frequency phonons are considered



to provide a majority of electron-phonon coupling strength as in the case of  $\text{MgB}_2$  [21]. However, some low-frequency modes show a marked change, either softening or line-broadening, upon cooling down to above  $T_c$  [22], which is a signature of strong electron-phonon coupling, not arising from FS nesting nor from phonon anharmonicity. Nevertheless, given that there is no insulating phase nearby and that 4d-Pd compound has higher  $T_c$  than 3d-Ni compound, superconductivity of this family is understood most likely by the type of phonon-mediated pairing without need for electronic pairing interactions nor correlation-induced enhancement of the electron-phonon coupling.

#### 2.4.4 Electron Doped $\beta\text{-HfNCl}$

Transition-metal chloronitrides  $\text{MNX}$  ( $\text{M}=\text{Ti, Zr, and Hf}$ ,  $\text{N}=\text{nitrogen}$ ,  $\text{X}=\text{Cl, Br, and I}$ ) form a fairly large family of superconductors. These materials are basically insulating, but electron doping makes them superconductors.  $T_c$  is 16 K for electron doped  $\text{ZrNCl}$  ( $\beta\text{-Li}_x\text{ZrNCl}$ ) [23] and the highest  $T_c=26$  K was recorded in 1998 for  $\beta\text{-Li}_x(\text{THF})_y\text{HfNCl}$  (THF stands for tetrahydrofuran) [24]. The crystal structure, shown in Fig. 2.4b, consists of (grapheme-like) honeycomb double sheets of alternating Hf and N. Each Hf (N) atom is bonded with three N (Hf) atoms within a layer. Layers of Cl on either side of this double sheet form an insulating block with charge neutral  $(\text{HfNCl})_2$  units. The neutral  $(\text{HfNCl})_2$  blocks are coupled each other via a weak van der Waals force along the  $c$  axis.

The chloronitrides have some features in common with  $\text{MgB}_2$ , such as layer structure and light element N. However, the LDA-based calculation yield the electron-phonon coupling  $\lambda \sim 0.5$  and  $\omega_m (\sim \sqrt{\langle \omega^2 \rangle}) \sim 36$  meV, giving  $T_c \sim 6$  K for the electron doped  $\text{ZrNCl}$  assuming  $\mu^*=0.1$  [25]. The calculated low  $T_c$  indicates either that an electronic pairing mechanism may be in operation or that electronic correlations (beyond LDA) may enhance the electron-phonon coupling as suggested for doped bismuthates. In fact, the doped MNCl's are metals with low carrier density in the normal state, and thus the screening effect is expected to be weak. An *ab initio* analysis using a DFT for SC non-empirically calculates both electron-phonon ( $\lambda$ ) and electron-electron ( $\mu^*$ ) interactions. The calculated  $\lambda$  is larger than 0.5 obtained by the LDA based calculation, but the screened/renormalized Coulomb interaction parameter  $\mu^*$  is found to be larger by a factor of about 2 than the commonly used empirical values (0.09–0.13). Because of the large  $\mu^*$  values, the resulting  $T_c$  values are low, below 10 K both for doped  $\text{ZrNCl}$  and  $\text{HfNCl}$  [26]. On the other hand, the calculations beyond LDA as is adapted to the doped bismuthates yield correlation-enhanced electron-phonon coupling  $\lambda \sim 1$ , giving  $T_c$ 's comparable with the experimental values, but they assume  $\mu^*=0.1$  [13]. The discrepancy between experiment and theory may be a signature for unconventional superconductivity. This remains open for future experiments and theories.

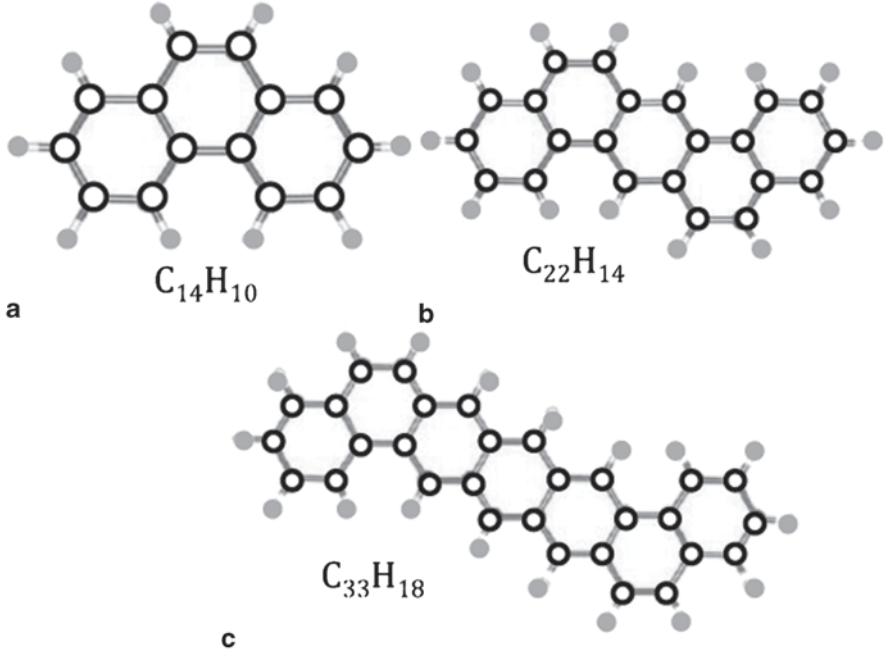


### 2.4.5 Doped Fullerides ( $C_{60}$ ) and Polycyclic-Aromatic-Hydrocarbons

Superconductivity of doped (alkaline ions (A) intercalated) fullerides ( $A_3C_{60}$ ) was discovered in 1991 [27]. Within a year  $T_c$  rose from 18 to 33 K by using larger alkaline ions as dopants [28]. In these fullerides  $C_{60}$  molecules build up a cubic fcc lattice. Since Cs has largest ionic radius,  $T_c$  for  $Cs_3C_{60}$  was expected to be higher. In fact, superconducting  $Cs_3C_{60}$  with  $T_c = 38$  K was synthesized in 2008 [29]. However, its crystal structure is not fcc but A15, a bcc packing of  $C_{60}$  with Cs-Cs pairs on the faces of the cubes (see Fig. 2.4c), and it is insulating at ambient pressure. Application of hydrostatic pressure transforms A15- $Cs_3C_{60}$  from insulator to superconductor at  $P \sim 4$  kbar. The maximum  $T_c = 38$  K is achieved at  $P \sim 7$  kbar.

Organic molecular SCs are one of the oldest “exotic” superconductors. The first discovered in 1980 was the one-dimensional (TMTSF)PF<sub>6</sub> showing SC with  $T_c = 0.9$  K under pressure of 12 kbar [30]. After several years  $T_c$  of organic SCs increased in the class of the organic charge transfer solids up to 13 K for the  $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl salt under pressure [31], but its increase stopped for more than 10 years before jumping up to 18 K in 2009. The newly discovered SC is a picene ( $C_{22}H_{14}$ ) which shows superconductivity at  $T_c = 18$  K at ambient pressure when doped (intercalated) with potassium [32]. The picene is composed of a hydrocarbon molecule with *five* benzene rings arranged in an “armchair” form and a member of a family of polycyclic aromatic hydrocarbons (PAH) (see Fig. 2.5). The K-doped phenanthrene ( $C_{14}H_{10}$ ) with *three* benzene rings is also a superconductor with  $T_c = 5$  K [33]. It is natural to expect a higher  $T_c$  for PAH with *seven* benzene rings. Recently,  $T_c \sim 30$  K has been reported for K-doped dibenzopentacene ( $C_{30}H_{18}$ ) [34]. However, the zero-resistance has not been confirmed yet.

A15- $Cs_3C_{60}$  as well as doped PAHs is narrow band metals. High electronic density of state at the Fermi energy  $N(E_F)$  and high phonon frequencies involving light C and H atoms may favor high  $T_c$ . Moreover, since they are in the proximity to an insulator-metal transition, the correlation-induced enhancement of the electron-phonon coupling may also be at work. On the other hand,  $E_F$  should be small and comparable with phonon energy  $\hbar\Omega_0$ , so they might be in the regime outside the Migdal-Eliashberg theory. A15- $Cs_3C_{60}$  is also an insulator at ambient pressure. The large inter  $C_{60}$  separation results in a reduction of the overlap between neighboring  $C_{60}$  molecules which produces a narrow band. The insulating states of both A15- $Cs_3C_{60}$  and undoped PAHs are likely Mott insulators due to electronic correlation  $U$  larger than the bandwidth  $W$ . The application of pressure would drive an insulator-metal transition by increasing the bandwidth. In this regard, superconductivity in doped  $C_{60}$  and PAH systems are marginal between phonon-mediated and electronic pairing.



**Fig. 2.5** Structural units of polycyclic aromatic hydrocarbons with 3 ( $C_{14}H_{10}$ ), 5 ( $C_{22}H_{14}$ ), and 7 ( $C_{30}H_{18}$ ) benzene rings. Picene with 5 rings becomes a superconductor with  $T_c = 18$  K upon electron doping [32]

## 2.5 Materials with Unconventional Pairing

Dominant pairing interaction, either electron-phonon or electron-electron, is yet to be determined for  $\beta$ -HfNCI,  $A_3C_{60}$ , and doped picene. On the other hand, the cuprates, heavy fermions compounds, iron pnictides/chalcogenides, and possibly some class of the organic superconductors are obviously superconductors with Cooper pairs formed by electronic pairing interactions derived from purely repulsive Coulomb interactions. This is evidenced by the unconventional SC pairing with sign-changing/anisotropic order parameter (SC gap). The  $d$ -wave gap is established for the cuprates with the maximum  $T_c^{\max} = 135$  K at ambient pressure, and the gap symmetry for most of iron-based superconductors with  $T_c^{\max} = 55$  K is either  $s_{\pm}$  or nodal  $s$  (or  $d$ -wave) depending on the material and doping level.  $T_c$ 's and their physics will be discussed in details in the next two Chapters.

The heavy-fermions (HF) superconductors, first discovered for  $CeCu_2Si_2$  in 1980 [35], are one of the representative strongly correlated electron systems. Their  $T_c$ 's are basically very low,  $T_c < 1$  K. Exceptionally, one of the HF families, the 115 family ( $CeMIn_5$  and  $PuMGa_5$  where  $M = Co, Ir, \text{ or } Rh$ ), show unusually high  $T_c$ .

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