Superconducting materials.

Main references:
W. Buckel, R. Kleiner
"Superconductivity - Fundamentals and Applications", 2nd Ed.
Wiley, 2004
K. Fossheim, A. Sudbø
"Superconductivity - Physics and applications", John Wiley and Sons,
Ltd, 2004

Superconductors

- Elements
- Binary Alloys
- MgB_2
- Cuprates
- Chevrel phases, Borocarbides
- Ruthenates, oxides
- Organic superconductors
- Fullerides
- Pnictides
- Heavy fermions
- Artificial layered superconductors

Low T_c vs High T_c

"Conventional"
"Unconventional"

"Metallic"
"Oxides"

"Practical" vs.
"interesting"

all: Cooper pairs
(carriers with charge 2*e* or –2*e*)

Microscopic state: an anticipation

Cooper pairs: electrons (or holes) couple in *pairs*, by means of some weak attractive interaction.

"Conventional":

opposite spin ("spin singlet state"), S=0
and
zero angular momentum, L=0

"*s*-wave", isotropic wf

wf = wavefunction

"Unconventional":

opposite spin ("spin singlet state"), S=0
and
nonzero even angular momentum, e.g. L=2
(for S=0 and totally antisymmetric wf)

"*d*-wave", anisotropic wf

parallel spin ("spin triplet state"), S=1
and
nonzero odd angular momentum, e.g. L=1
(for S=1 and totally antisymmetric wf)

"*p*-wave", anisotropic wf

beware: the crystal field breaks the degeneracy
with respect to the free-space "atom"

Elements

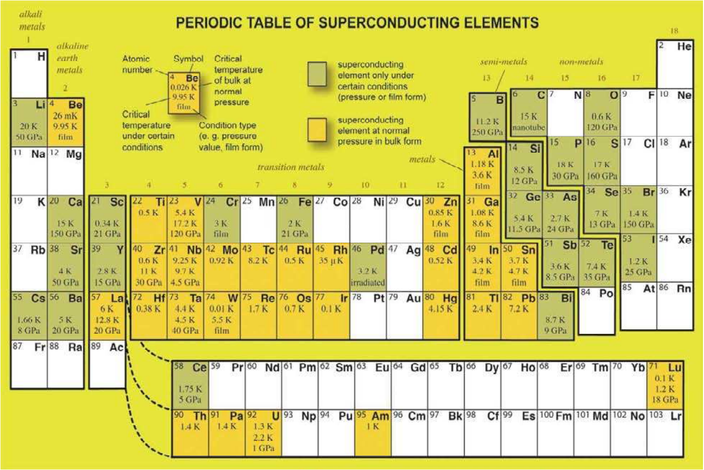


Figure 2. *Periodic table of superconducting elements*

Figure from
C. Buzea, K. Robbie
Supercond. Sci. Technol. 18 (2005) R1-R8,
preprint available at
http://arxiv.org/abs/cond-mat/0410302v1

Elements

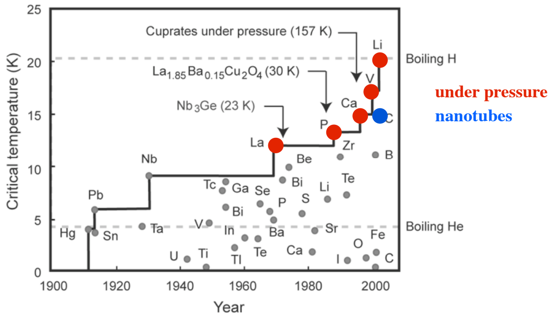


Figure 1. *Historical development of the critical temperature of simple elements*

The figure reports the maximum Tc, often at high pressure or in a strained or compressed form (thin film)

Figure from
C. Buzea, K. Robbie
http://arxiv.org/abs/cond-mat/0410302v1
published version:
Supercond. Sci. Technol. 18 (2005) R1-R8

Elements

	Element	T_c in K	Crystal structure	Melting point in °C	Θ_D in K	λ_L in nm	ξ_{GL} in nm	B_c in G
1	Al	1.19	k. f. z.	660	420	50	500–1600	100
2	Am [7]	0.8	hex.	994				
3	Be	0.026	hex.	1283	1160			
4	Cd	0.55	hex.	321	300	130	760	30
5	Ga	1.09	orth.	29.8	317	120		59
		(6.5; 7.5)						
6	Hf [8]	0.13	hex.	2220				
7	Hg	4.15	rhom.	−38.9	90		55	400
		(3.95)	tetr.					(340)
8	In	3.40	tetr.	156	109	24–64	360–440	280
9	Ir	0.14	k. f. z.	2450	420			19
10	La	4.8	hex.	900	140			
		(5.9)	k. f. z.					(1600)
11	Mo	0.92	k.r.z.	2620	460			98
12	Nb	9.2	k.r.z.	2500	240	32–44	39–40	1950
13	Np [9]	0.075	orth.					
14	Os	0.65	hex.	2700	500			65
15	Pa	1.3						
16	Pb	7.2	k. f. z.	327	96	32–39	51–83	800
17	Re	1.7	hex.	3180	430			190
18	Rh [10]	3.2×10^{-4}	k. f. z.	1966	269			
19	Ru	0.5	hex.	2500	600			66
20	Sn	3.72	tetr.	231.9	195	25–50	120–320	305
		(5.3)	tetr.					
21	Ta	4.39	k.r.z.	3000	260	35	93	800
22	Tc	7.8	hex.		351			177
23	Th	1.37	k. f. z.	1695	170			150
24	Ti	0.39	hex.	1670	426			100
25	Tl	2.39	hex.	303	88			170
26	U (α)	0.2	orth.	1132	200			
27	V	5.3	k.r.z.	1730	340	39.8	45	1200
28	W	0.012	k.r.z.	3380	390			1.24
29	Zn	0.9	hex.	419	310		25–32	52
30	Zr	0.55	hex.	1855	290			47

k.f.z. = fcc
k.r.z. = bcc

Physical properties: very different from each other (crystal structure, Debye temperature,....

No evident pattern linking normal state properties and superconductivity.

BUT
when different crystal structures exists for the same superconducting element, T_c changes with structure.

Magnetic compounds: no superconductivity found.

Hint: magnetic order (thermodynamic phase) *different* and *competitive* with superconducting order

Noble metals and copper: no superconductivity found.
Hint: very low electron-phonon interaction (= high conductivity) is an obstacle to superconductivity.

Table from
W. Buckel, R. Kleiner
"Superconductivity - Fundamentals and Applications", 2nd Ed.
Wiley, 2004

Elements: applications

T_c : 0.32 mK (Rh) ÷ 9.2 K (Nb)
(ambient pressure; under pressure Li, e.g., has $T_c \approx 20$ K).

$\mu_0 H_c(0)$: 0.1 (W) ÷ 2000 (Nb) mT

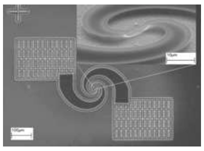
Mostly Type–I superconductors
Notable exception: Nb

$\Longrightarrow$

No power applications.
Signal applications: partially.

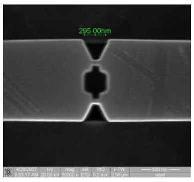
Pb, Nb: SQUIDS

Nb: high-frequency applications



Nb superconducting bolometer
https://www.jyu.fi/fysiikka/en/research/material/nanophys/thermal/detector.html

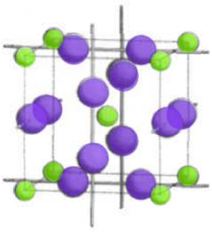
rf cavity for linac, Cornell University
Q (1.8K) ≈ $2 \cdot 10^{11}$
http://www.lns.cornell.edu/~liepe/webpage/news.html



Nb SQUID with the loop size of 300 nm and the constriction width of 60 nm.
http://www.npl.co.uk/quantum-phenomena/nanophysics/research/magnetic-sensors

Binary alloys

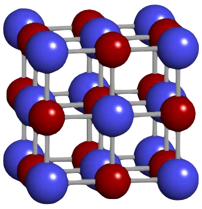
β-tungsten or A15 compounds: A_3B



Exercise:
verify the
stoichiometry

Examples: Nb_3Sn, Nb_3Ge, V_3Si

Solid solutions



Examples: NbTi, NbN

Type II superconductors.
Often high upper critical field H_{c2}.

Binary alloys

Type II superconductors.
High upper critical field H_{c2}.

Technological superconductors

Table 2.2 Some binary alloys and stoichiometric compounds. Values of T_c and $B_{c2}(0)$ may vary somewhat depending on precise composition

Compound	T_c [K]	$B_{c2}(0)$ [T]
V_3Si	17	25
Nb_3Sn	18	24
Nb_3Ge	23.2	38
V_3Ga	14	21
NbTi	9	15
VTi	7	11
NbN	16	16

Table from
K. Fossheim, A. Sudbø
"Superconductivity - Physics and applications", John Wiley and Sons, Ltd, 2004

Matthias Rule

EMPIRICAL!

The average number of valence electrons (defined as all the electrons in non-closed shells) of a material dictates the presence of superconductivity and the optimization of T_c.

The rule keeps validity for alloys.

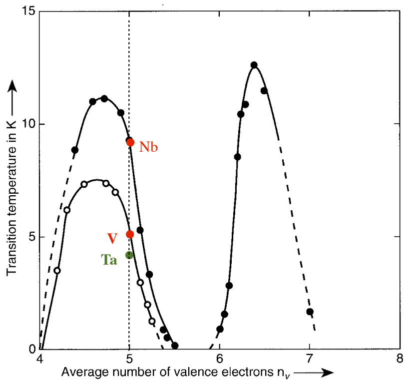


Fig. 2.2 Transition temperature of some alloys of the transition metals plotted versus the average number of valence electrons (from [26]): solid dots, Zr-Nb-Mo-Re; open circles, Ti-V-Cr.

Figure from
W. Buckel, R. Kleiner
"Superconductivity - Fundamentals and Applications", 2nd Ed.
Wiley, 2004

Alloys: applications

$T_c > 4$ K

$\mu_0 H_{c2}(0)$ up to ~25 T

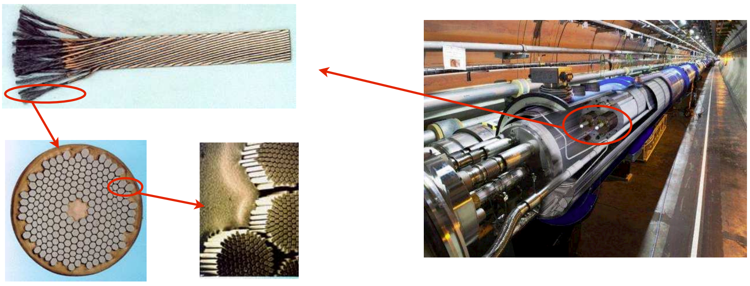
Type–II superconductors

$\Longrightarrow$

Power applications.

Signal applications: partially.
(NbN tunnel junctions)

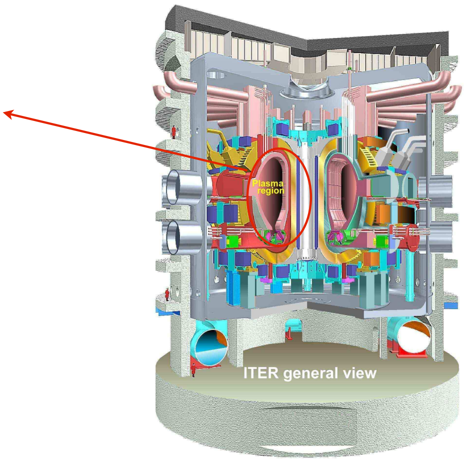
Alloys: applications



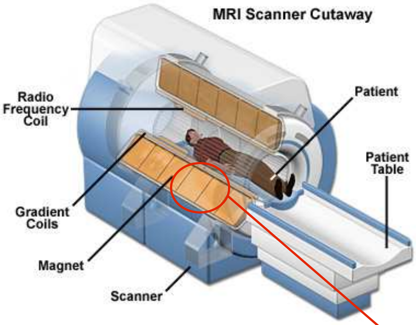
NbTi Cables for LHC
http://lhc-machine-outreach.web.cern.ch/lhc-machine-outreach/components/cable.htm

Alloys: applications

Nb3Sn Cables for ITER magnets
http://www.fusione.enea.it/SUPERCOND/nb3sn.html.en



Alloys: applications



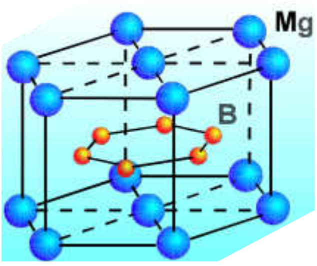
Magnets for Magnetic Resonance Imaging
http://www.magnet.fsu.edu/education/tutorials/magnetacademy/mri/fullarticle.html

Superconducting solenoid

etc etc etc….!

MgB_2

Discovered 2001.
Type II superconductor.
"Two-band".
Anisotropic
$T_c = 40$ K
$H_{c2}(0) \approx 20 \div 40$ T (along the planes)



Metallic, can be pressed into cables.
Useful for cryogenerator-based applications (no LHe)

Cuprates

Discovered 1986.
Type II superconductor.

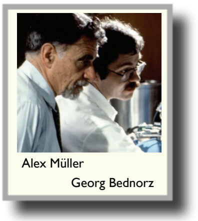
Strongly anisotropic: with respect to different crystal orientation, ("*ab* planes" and "*c* axis"):

- normal state resistivity changes by a factor up to 10^5 (in BiSrCacuO)!
- H_{c2}, λ_L, ξ, change by a factor ~7 (YBaCuO) ÷ ~200 (BiSrCacuO)

Doped oxides (not simple metals!)
Dozens of compounds.

T_c up to 133 K (164 K under pressure)
$H_{c2}(0) \approx 300$ T (along the planes)

Unusual microscopic state:
d-wave (L=2).
Wavefunction anisotropic.



(Nobel 1987)

Table 2.7 Some representative examples of high-T_c cuprate superconductors and their T_c's. The reported values of T_c will vary somewhat, depending on the processing conditions and resulting oxygen content and other deviations from stoichiometry

Compound	T_c [K]	Nicknames
$La_{1.85}Sr_{0.15}CuO_4$	39	LCCO or LaSCCO
$YBa_2Cu_3O_7$	92	Y123 or YBCO
$Bi_2Sr_2CaCu_2O_8$	← 84	Bi2212 or BiSCCO
$Bi_2Sr_2Ca_2Cu_3O_{10}$	← 110	Bi2223 or BiSCCO
$Tl_2Ba_2CuO_6$	90	
$Tl_2Ba_2CaCu_2O_8$	110	
$Tl_2Ba_2Ca_2Cu_3O_{10}$	125	Tl2223 or TBCCO
$TlBa_2CaCu_2O_7$	91	
$TlBa_2Ca_2Cu_3O_9$	116	
$TlBa_2Ca_3Cu_4O_{11}$	122	
$HgBa_2CuO_4$	95	
$HgBa_2CaCu_2O_6$	122	
$HgBa_2Ca_2Cu_3O_8$	133	Hg1223 or HBCCO
$Nd_{1.85}Ce0.15CuO_{4-y}$	25	NCCO

Table from
K. Fossheim, A. Sudbø
"Superconductivity - Physics and applications", John Wiley and Sons, Ltd, 2004

Cuprates

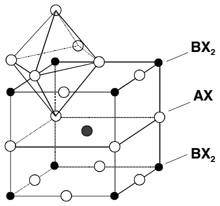
Table 2.7 Characteristic data of different cuprate superconductors: maximum transition temperature, magnetic penetration depths λ_{ab} and λ_c for applied magnetic fields perpendicular and parallel to the layers, respectively, as well as the Ginzburg-Landau coherence lengths ξ_{ab} and ξ_c parallel and perpendicular to the CuO_2 layers, respectively. Also the upper critical fields for field orientations perpendicular and parallel to the planes, respectively, are given. In some cases, at low temperatures the upper critical fields are extremely high, and frequently they were extrapolated to low temperatures from the slope dB_{c2}/dT near the transition temperature.

Composition	$T_{c,max}$ in K	λ_{ab} in nm	λ_c in µm	ξ_{ab} in nm	ξ_c in nm	$B_{c2\perp}$ in T	$B_{c2\parallel}$ in T	Reference
$La_{1.83}Sr_{0.17}CuO_4$	38	100	2–5	2–3	0.3	60		[87]
$YBa_2Cu_3O_{7-x}$	93	150	0.8	1.6	0.3	110	240	[88, 89]
$Bi_2Sr_2CuO_{6+x}$	13	310	0.8	3.5	1.5	16–27	43	[90]
$Bi_2Sr_2CaCu_2O_{8+x}$	94	200–300	15–150	2	0.1	>60	>250	[87]
$Bi_2Sr_2Ca_2Cu_3O_{10+x}$	107	150	>1	2.9	0.1	40	>250	[91]
$Tl_2Ba_2CuO_{6+x}$	82	80	2	3	0.2	21	300	[92–94]
$Tl_2Ba_2CaCu_2O_{8+x}$	97	200	>25	3	0.7	27	120	[91, 92, 95]
$Tl_2Ba_2Ca_2Cu_3O_{10+x}$	125	200	>20	3	0.5	28	200	[96, 97]
$HgBa_2CuO_{4+x}$	95	120–200	0.2–0.45	2	1.2	72	125	[98]
$HgBa_2CaCu_2O_{6+x}$	127	205	0.8	1.7	0.4	113	450	[98]
$HgBa_2Ca_2Cu_3O_{8+x}$	135	130–200	0.7	1.5	0.19	108		[98–100]
$HgBa_2Ca_3Cu_4O_{10+x}$	125	160	7	1.3–1.8		100	>200	[101, 102]
$Sm_{1.85}Ce_{0.15}CuO_{4-y}$	11.5			8	1.5			[103]
$Nd_{1.84}Ce_{0.16}CuO_{4-y}$	25	72–100		7–8	0.2–0.3	5–6	>100	[104, 105]

Table from
W. Buckel, R. Kleiner
"Superconductivity - Fundamentals and Applications", 2nd Ed.
Wiley, 2004

Cuprates: structure

Double perovskite



Example: La_2CuO_4

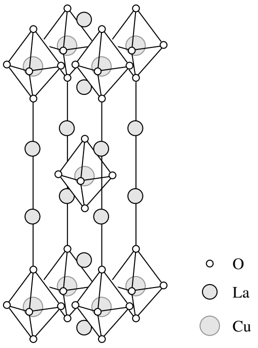


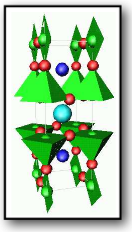
Figure from
W. Buckel, R. Kleiner
"Superconductivity - Fundamentals and Applications", 2nd Ed.
Wiley, 2004

Figure from
K. Fossheim, A. Sudbø
"Superconductivity - Physics and applications", John Wiley and Sons, Ltd, 2004

$YBa_2Cu_3O_7$: structure

Complex structure.

Note the CuO double planes.



Exercise: verify the stoichiometry

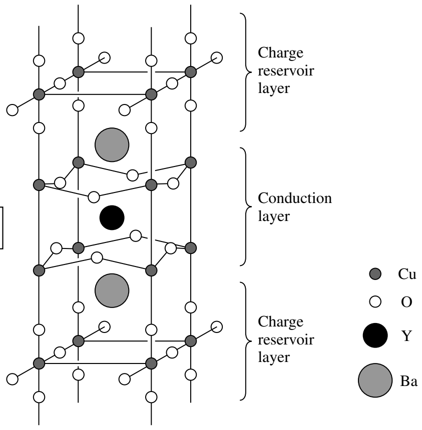


Figure 2.10 Structure of orthorhombic $YBa_2Cu_3O_7$.

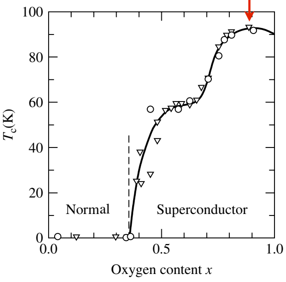
Figure from
K. Fossheim, A. Sudbø
"Superconductivity - Physics and applications", John Wiley and Sons, Ltd, 2004

$YBa_2Cu_3O_7$: T_c vs. doping

VERY puzzling phase diagram.

Hole (super)conductor.
Cooper pairs (experiment on flux quantization)
T_c changes with O content:
$YBa_2Cu_3O_{6+x}$
or also
$YBa_2Cu_3O_{7-\delta}$

Optimum T_c : $x \neq 1$



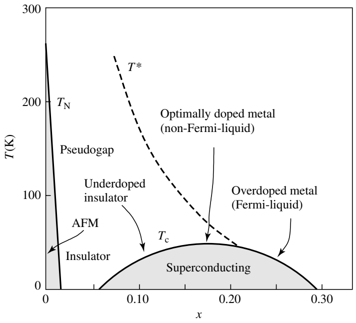


Figure 2.15 Typical overall phase diagram with doping in high-T_c cuprate superconductors (AFM = antiferromagnetic phase).

Figures from
K. Fossheim, A. Sudbø
"Superconductivity - Physics and applications", John Wiley and Sons, Ltd, 2004

$Bi_2Sr_2CaCu_2O_8$

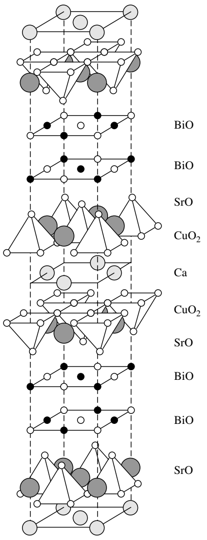


Figure 2.14 Structure of $Bi_2Sr_2CaCu_2O_8$ crystal.

Anisotropy: extreme.
Quasi-2D

Figure from
K. Fossheim, A. Sudbø
"Superconductivity - Physics and applications", John Wiley and Sons, Ltd, 2004

Structure (alternative view)

Note the quasi-2D CuO planes + separating blocks

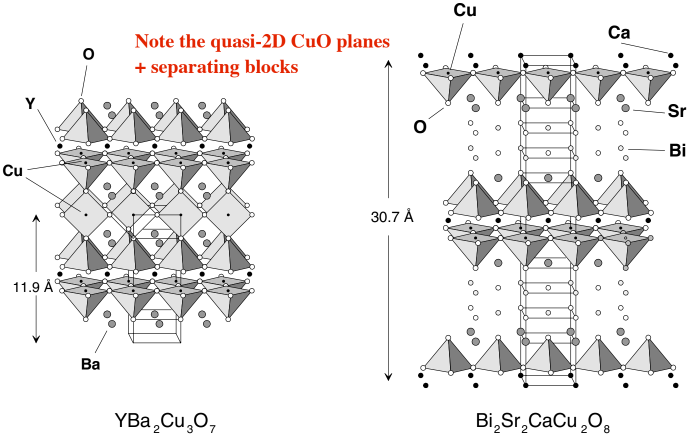


Fig. 2.13 Crystal structures of the two high-temperature superconductors $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$.

Figure from
W. Buckel, R. Kleiner
"Superconductivity - Fundamentals and Applications", 2nd Ed.
Wiley, 2004

Cuprates: applications

- High H_{c2}, high J_c: power applications.
- Cables, magnets
- Transformers, Fault current limiters

- Signal applications: SQUIDS, microwave filters, ...

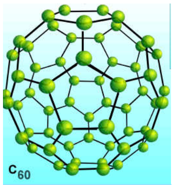
A new era in superconducting applications!

Fullerides

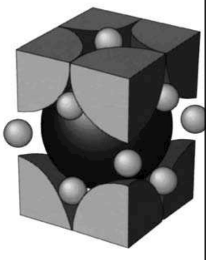
Doped with interstitial alkali metals

High $T_c \sim 40$ K.
High $H_{c2} \sim 50$ T

No applications.
Interesting as "very high T_c BCS superconductors"



Fullerene molecule
("Buckyball")



(b)

(b) Crystal structure of the fullerides [46].

Table 2.5 Structure and T_c's of some fullerene type superconductors

Material	Symmetry of the salts	T_c[K]
K_3C_{60}	fcc	19.3
Cs_2RbC_{60}	fcc	33
$(NH_3)_4Na_2CsC_{60}$	fcc	29.6
Cs_3C_{60}	bct/bcc	40
$NH_3K_3C_{60}$	Orthorhombic	28
Rb_x(OMTTF)C_{60} (benzene)		26

fcc = face-centered cubic, bct = body-centered tetragonal, bcc = body-centered cubic, OMTTF = octamethylenetetrathiafulvalene.

Table from
K. Fossheim, A. Sudbø
"Superconductivity - Physics and applications", John Wiley and Sons, Ltd, 2004

Figure from
W. Buckel, R. Kleiner
"Superconductivity - Fundamentals and Applications", 2nd Ed.
Wiley, 2004

Organic superconductors

Linear chains, quasi-2D

Anisotropy along three axes

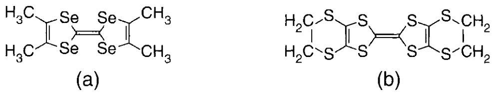


Fig. 2.17 Structural formulas of organic superconductors: (a) tetramethyltetraselenofulvalene (TMTSF); (b) bis(ethylenedithia)tetrathiafulvalene (BEDT-TTF).

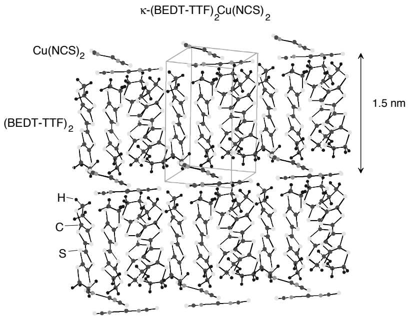


Fig. 2.18 Crystal structure of the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [124].

Table 2.8 Data of some organic superconductors based on the BEDT molecule: maximum transition temperature $T_{c,max}$, magnetic penetration depths $\lambda_\perp$ and $\lambda_\parallel$ for magnetic field orientations perpendicular and parallel to the layers, respectively, and the Ginzburg-Landau coherence lengths $\xi_\parallel$ and $\xi_\perp$ perpendicular and parallel to the layers, respectively. The upper critical fields for field orientations perpendicular and parallel to the layers are also indicated. (Data mostly from [M12].)

Composition	$T_{c,max}$ in K	$\lambda_\perp$ in nm	$\lambda_\parallel$ in μm	$\xi_\parallel$ in nm	$\xi_\perp$ in nm	$B_{c2\perp}$ in T	$B_{c2\parallel}$ in T
κ-(BEDT-TTF)$_2$Cu(NCS)$_2$	10.4	500–2000	40–200	5–8	0.8	6	30–35
(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br	11.2	550–1500	40–130	2.5–6.5	0.5–1.2	8–10	80
β$_H$-(BEDT-TTF)$_2$I$_3$	7–8*			12.5	1	2.7	25
β$_L$-(BEDT-TTF)$_2$I$_3$	1.5	3500	30–40	60–63	2.0	0.08	1.7–1.8
β-(BEDT-TTF)$_2$IBr$_2$	2.2	550	4–5	44–46	1.9	3.3–3.6	1.5
β-(BEDT-TTF)$_2$AuI$_2$	4.2	500	4	18–25	2–3	6.1–6.6	

* At a pressure of 1.6 kbar.

Figures from
W. Buckel, R. Kleiner
"Superconductivity - Fundamentals and Applications", 2nd Ed.
Wiley, 2004

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and other superconducting animals...

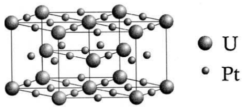
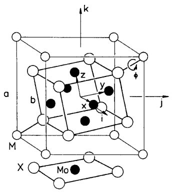


Fig. 2.10 Crystal structure of the heavy-fermion superconductor UPt$_3$ [65].

Heavy Fermions

- effective masses $m^* \sim 10^{2 \div 3}\, m_e$
- extreme type II
- Low T_c, moderate H_{c2}.
- Magnetic interaction



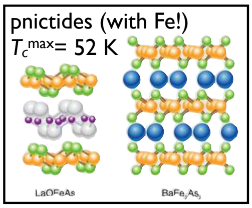
Chevrel phases

- MMo_6X_8, with M=metal, rare earth; X=S, Se
- extreme type II
- Low T_c, low to very high H_{c2}.
- Rare earths: magnetic order competes with superconductivity (e.g., H_{c2} nonmonotonic)

Boron carbides

Ruthenates

...


pnictides (with Fe!)
$T_c^{max} = 52$ K