High-Tc Superconductivity

by Metallizing Strong-bonding Electrons

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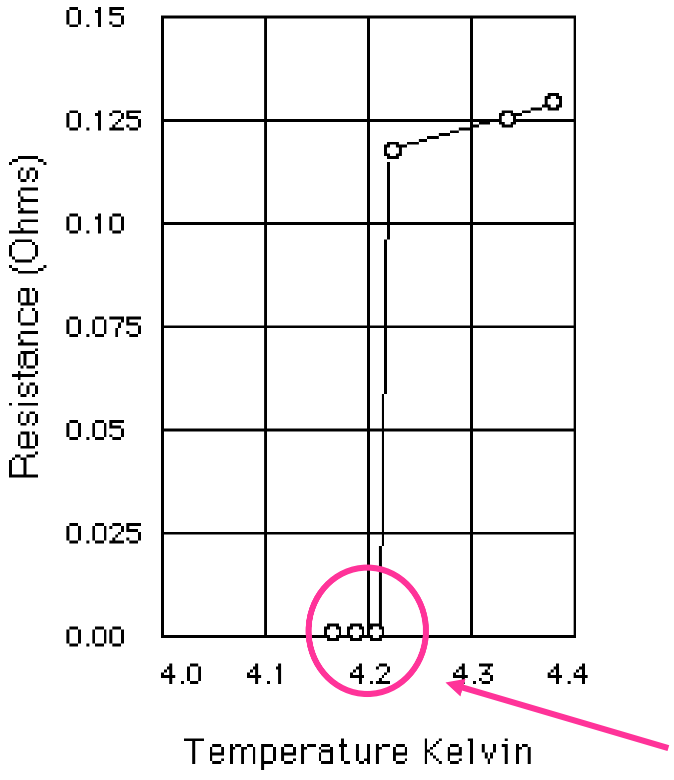
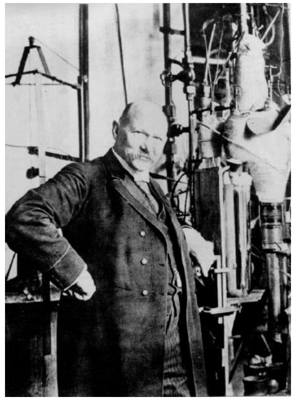
What is superconductor?

Ideal Conductor: zero resistance

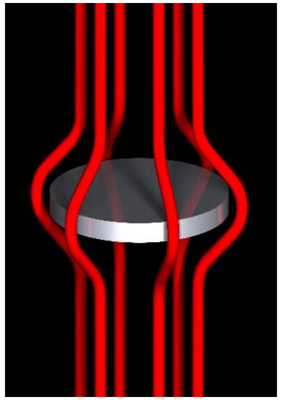




Heike Kamerlingh Onnes

Critical temperature

Ideal Diamagnet: Messiner Effect



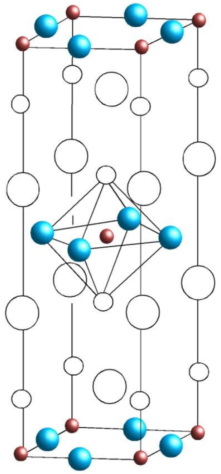
Walther Meissner

High-Tc Superconductors Discovered

It is not difficult to find superconductors

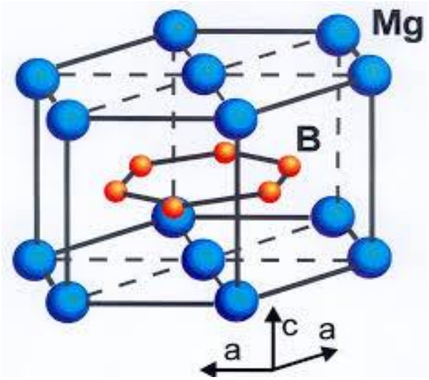
But it is difficult to find high-Tc superconductors

30~160 K



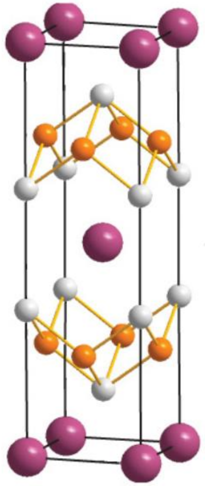
Cuprate SC

39 K



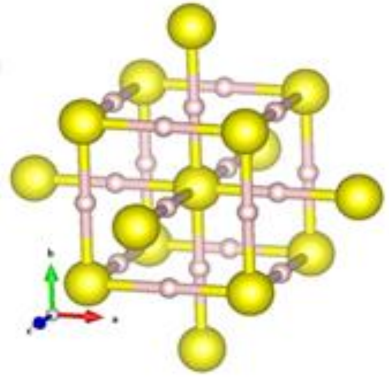
MgB_2

30~56 K



Iron-based SC

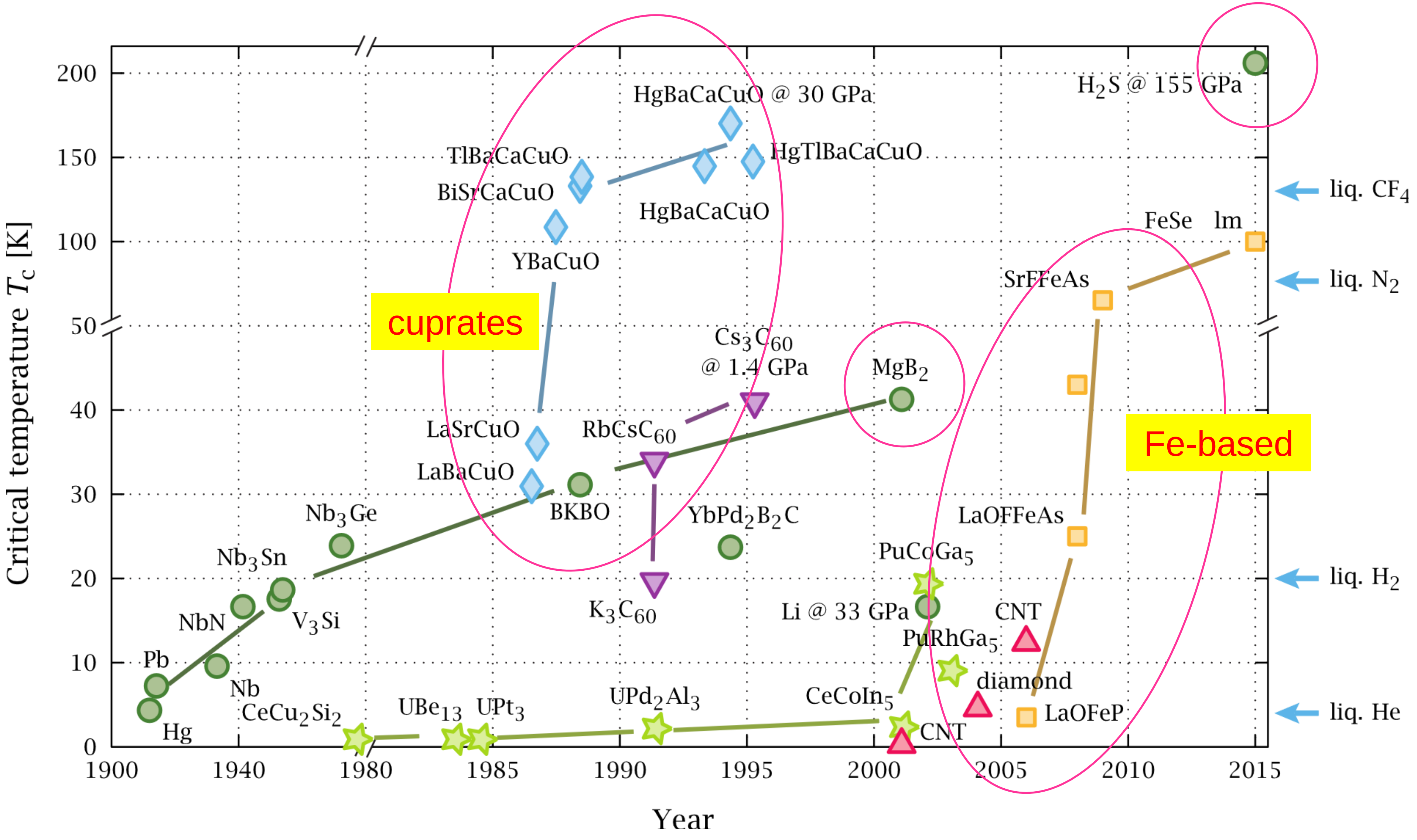
100~280K



H_3S and other H-enriched SC

Superconducting transition temperature ~ 40 K or higher

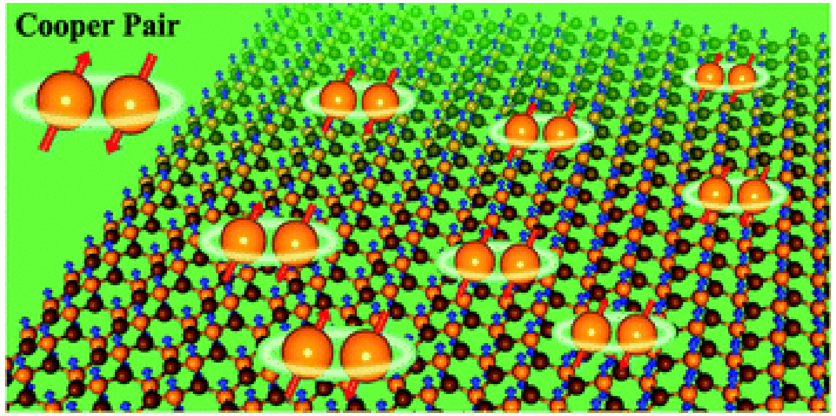
Timeline of Discovered Superconductors



By PJRay, https://commons.wikimedia.org/w/index.php?curid=4619314

How to become a superconductor?

Bardeen Cooper Schrieffer
1957 / 1972



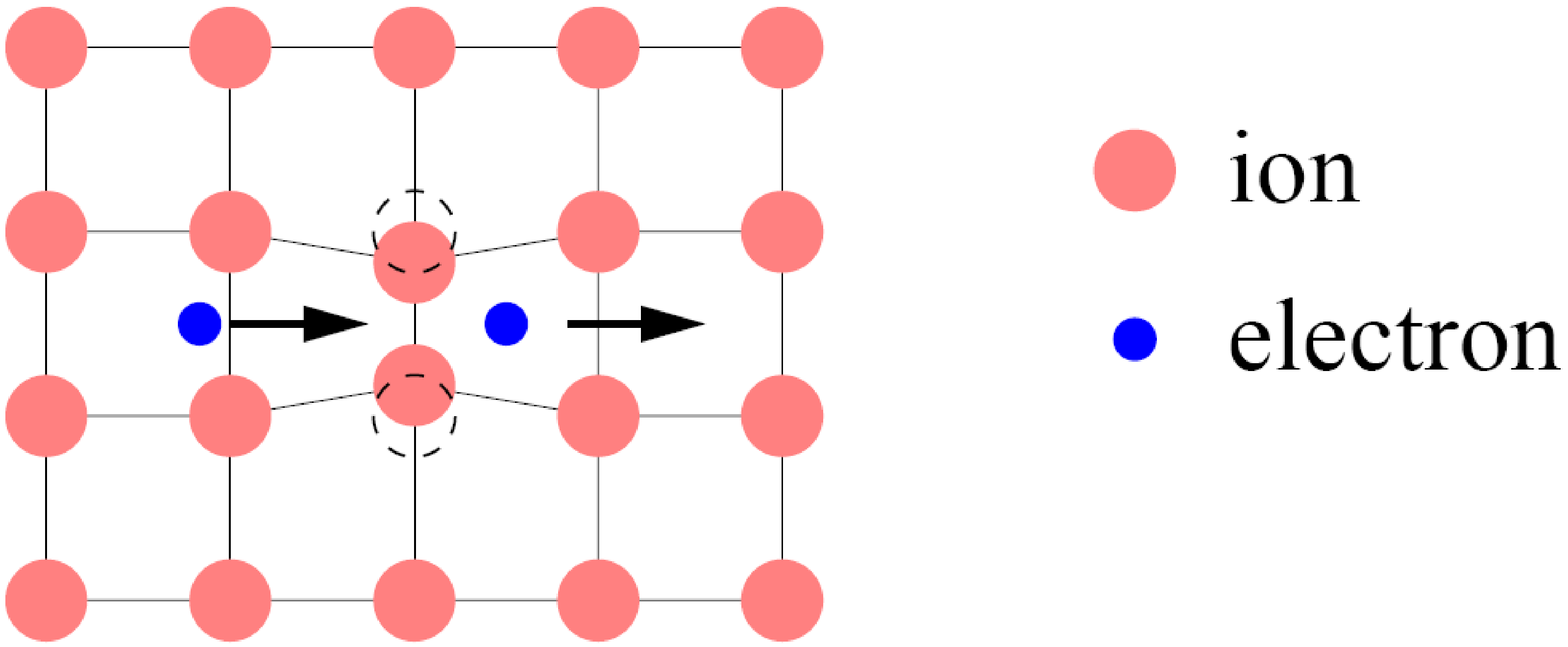
1. Electrons must form Cooper pairs: any two electrons should form a bound state

Binding energy of Cooper pair Δ determines the transition temperature T_c

Larger Δ, higher T_c

2. Cooper pairs must condense to form phase coherence

How can electrons form Cooper pairs? Typical Picture



Polarization of the lattice by one electron leads to an attractive potential for another electron, which binds two electrons to a bound state

Is there any guiding principle for hunting superconductors

Bernd Matthias rules：

1. high symmetry is good, cubic symmetry is the best
2. high density of electronic states is good
3. stay away from oxygen
4. stay away from magnetism
5. stay away from insulators
6. stay away from theorists.

Wrong except the 6th rule

Cava’s rule:

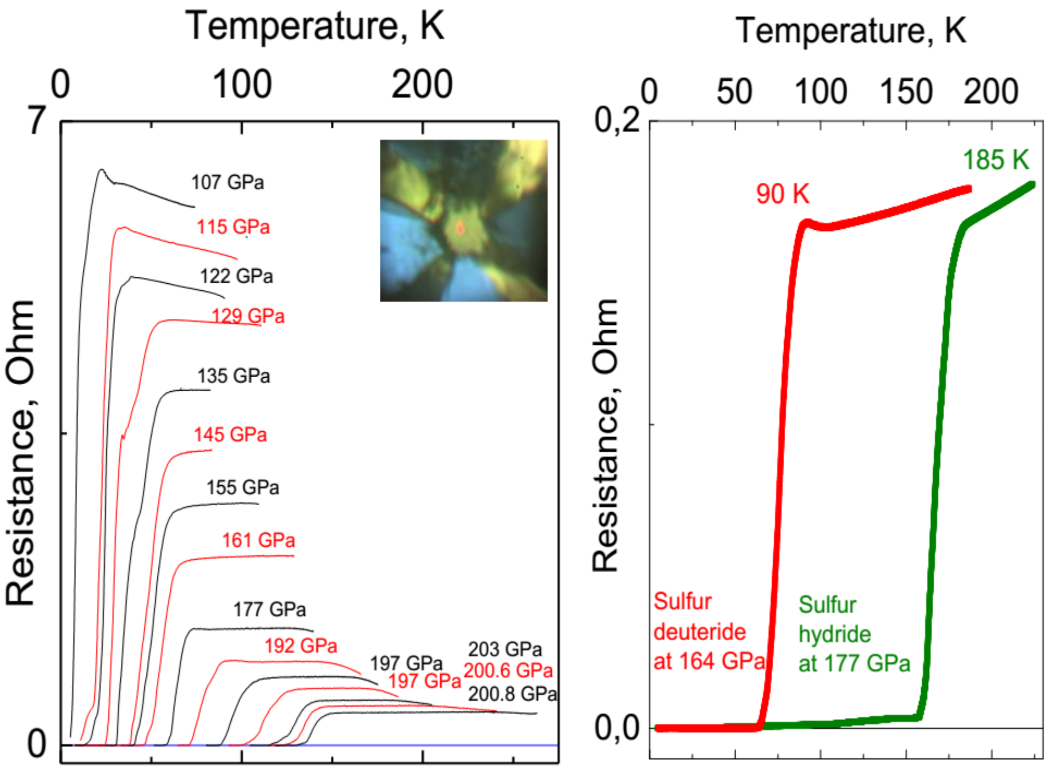
发现的超导体的临界温度和发现者经验的指数成反比

Conventional Wisdom of Raising T_c

To apply high pressure to light elements

Example: H enriched H_3S

1. T_c decreases with magnetic field
2. strong isotope shift of T_c in D_2S: Tc 185 K for H_2S, 90 K for D_2S



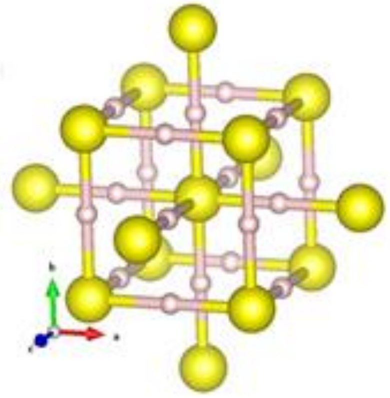
AP Drozdov, MI Eremets, IA Troyan, Nature 2015

Conventional Wisdom of Raising T_c

To apply high pressure to light elements

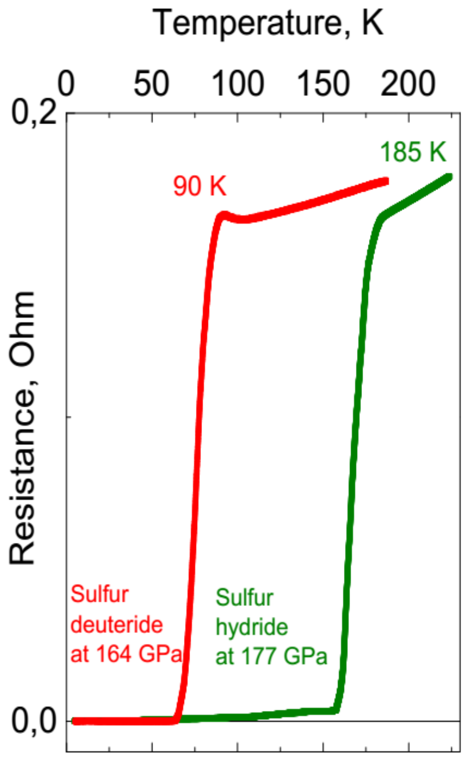
H enriched H_3S: possible 190K superconductor at 200 GPa

λ	ω_{log}	μ^*	T_c	*Pressure*
2.19	*1334.6* K	0.1~0.13	191-204 K	200 GPa
		0.13	184 K	250 GPa
		0.13	179 K	300 GPa



H_3S

Agree with DFT prediction for H_3S



D. Duan *et al.*, Sci. Reports 4, 6968 (2014)

How to Hunt High-Tc Superconductors

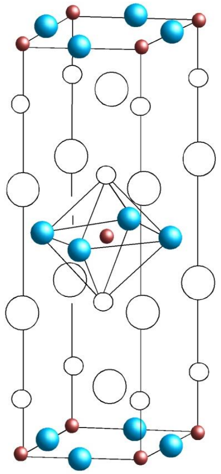
Guiding Principle:

There is a big chance to find high-Tc superconductors if one can metallize σ- or other strong chemical bonding electrons

Common Features of High-Tc Superconducts Revealed

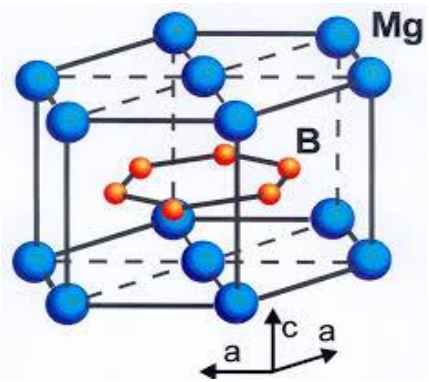
Cuprates still hold the record of highest-Tc at ambient pressure

30~160 K



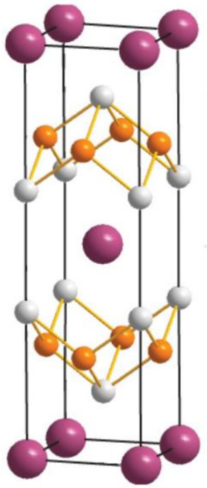
Cuprate SC

39 K



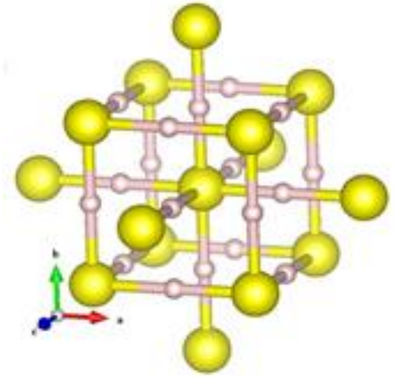
MgB_2

30~56 K



Iron-based SC

100~280K



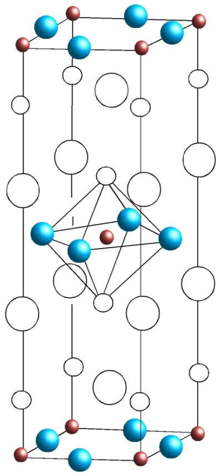
H_3S and other
H-enriched SC

Common Features of High-Tc Superconducts Revealed

Quasi-two-dimensional?

Yes

30~160 K



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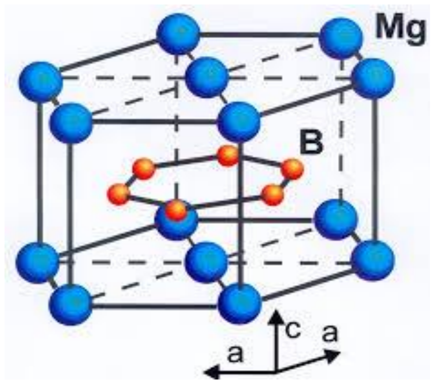

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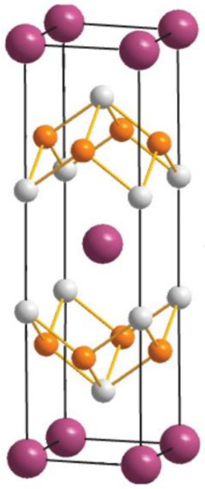
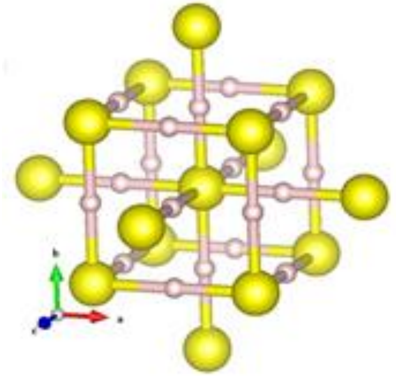


Iron-based SC

No

100~280K



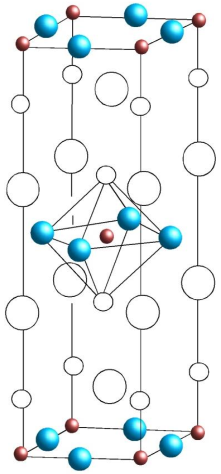
H_3S and other H-enriched SC

Common Features of High-Tc Superconducts Revealed

Strong antiferromagnetic fluctuations?

Yes

30~160 K



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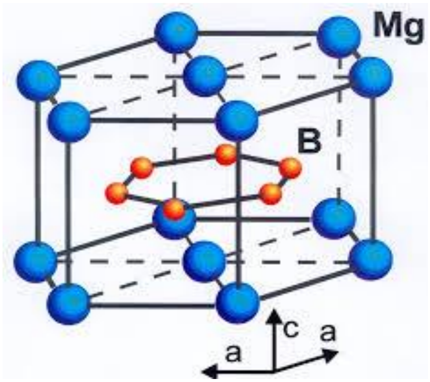
No

39 K



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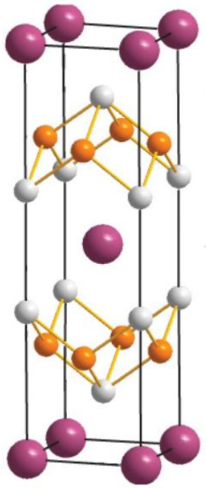

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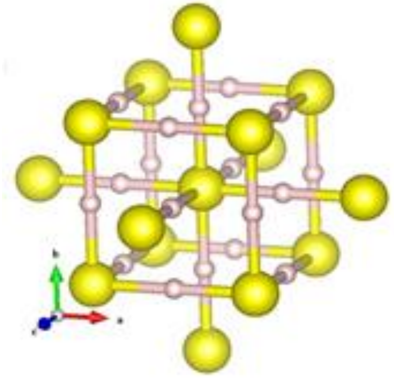


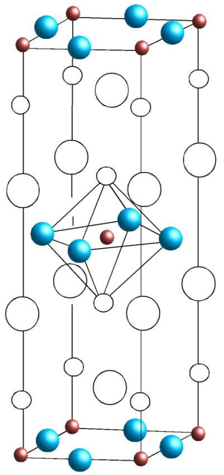
H_3S and other H-enriched SC

Common Features of High-Tc Superconducts Revealed

Strong electron-phonon coupling?

probably

30~160 K



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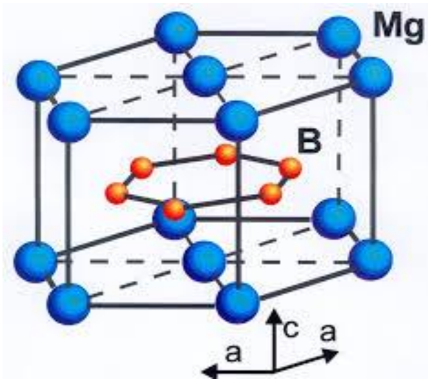

MgB_2

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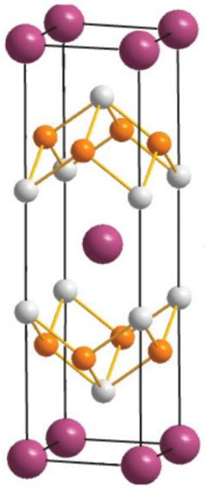

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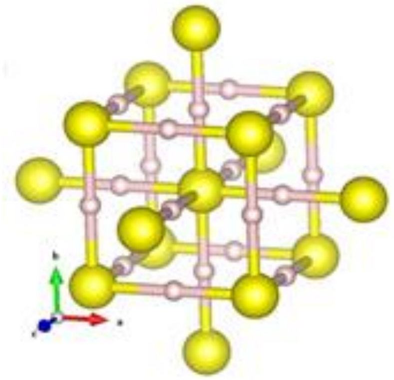


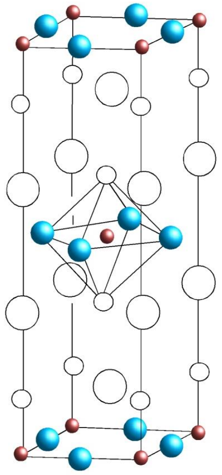
H_3S and other H-enriched SC

Common Features of High-Tc Superconducts Revealed

Some σ-bonding electrons become metallized?

Yes

30~160 K



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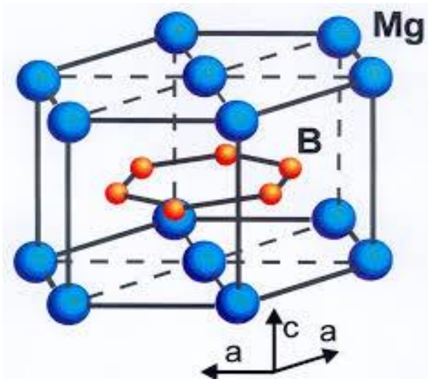

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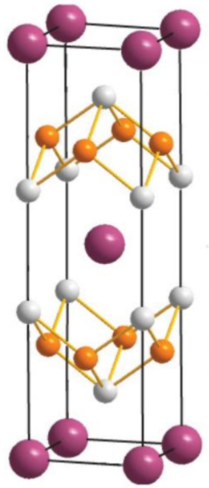

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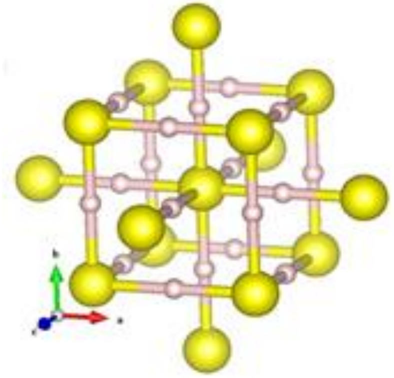
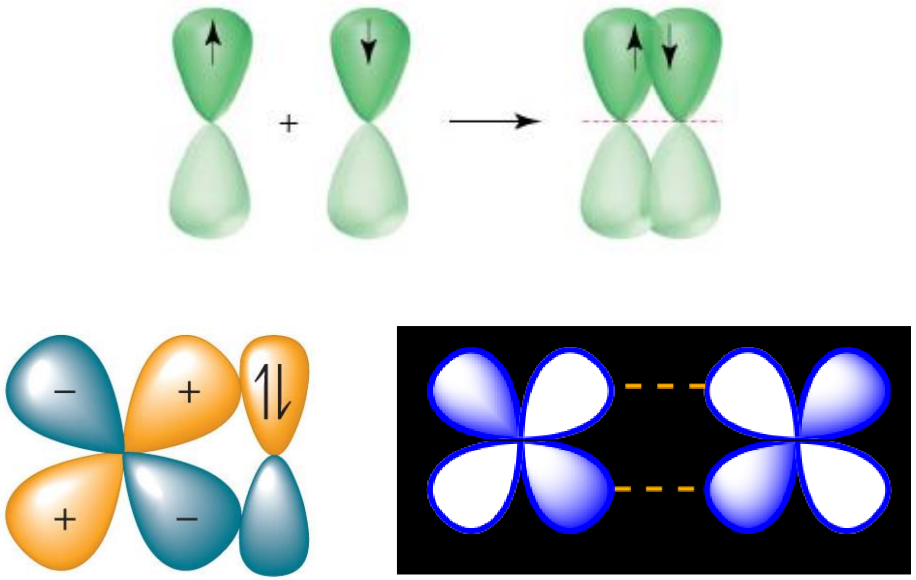


H_3S and other
H-enriched SC

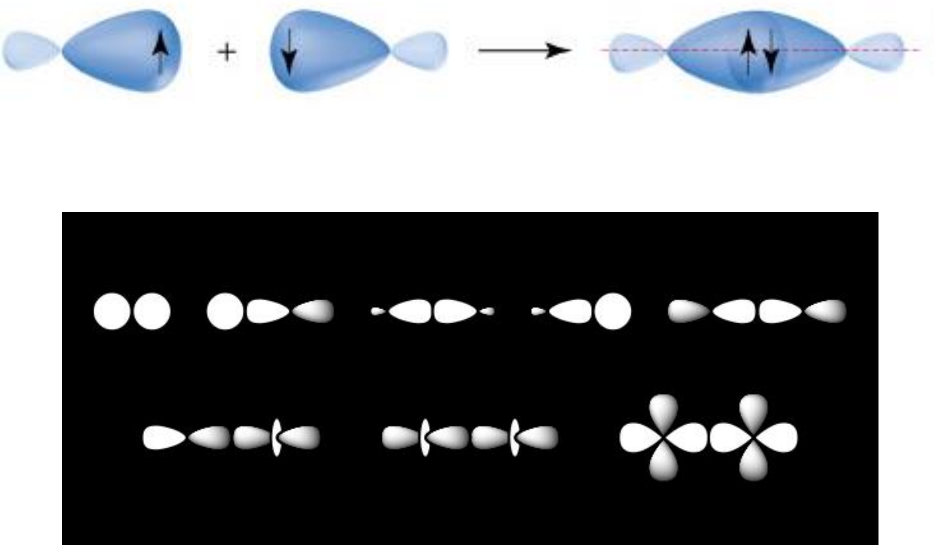
What are σ-bonding electrons?

π-bond: Sideways overlap



σ-bond: Head-on overlap

strongest covalent bonds



Crystal structure is generally stabilized by σ-bonds

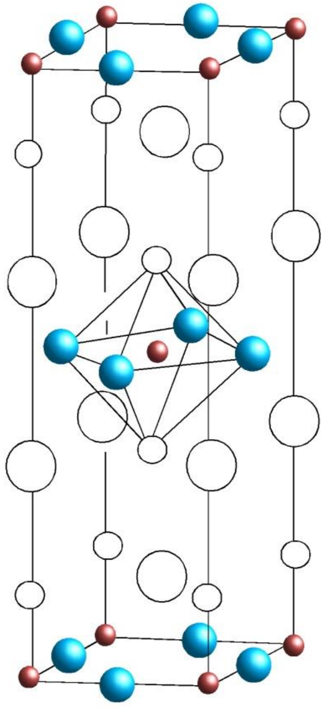
Metallizing σ-bonding electrons generally mean melting the lattice

Why are σ-bonding electrons relevant to high-Tc SC?

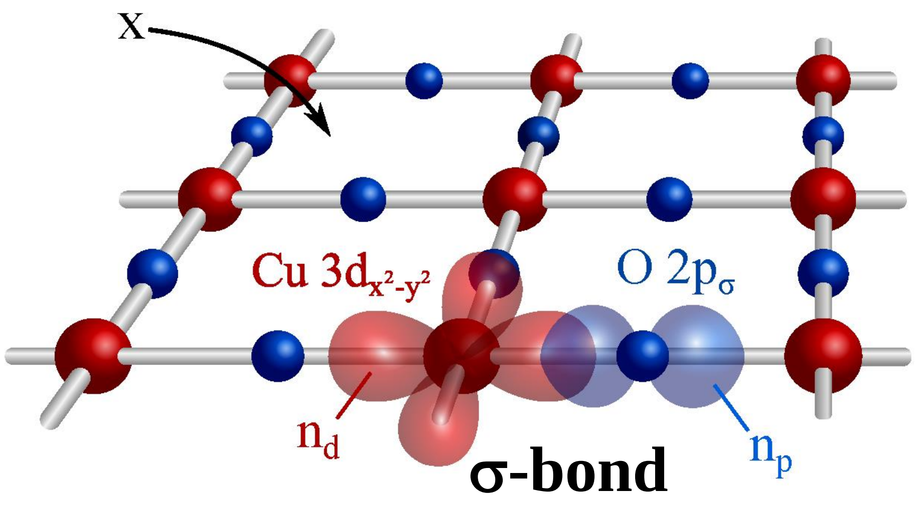
- **Characteristic energy scale of σ-bond is very strong: ~ 3 eV**
  1. **the coupling between σ-bonding electrons and phonons is very strong in order to stabilize this bond**
  2. **σ-electrons are difficult to be metallized: this explains why high-Tc SC are so difficult to find**

- **Metallzing σ-electrons reduces the coupling of these electrons, but the residual interaction can still be very large, which serves as a strong glue of Cooper pairs**

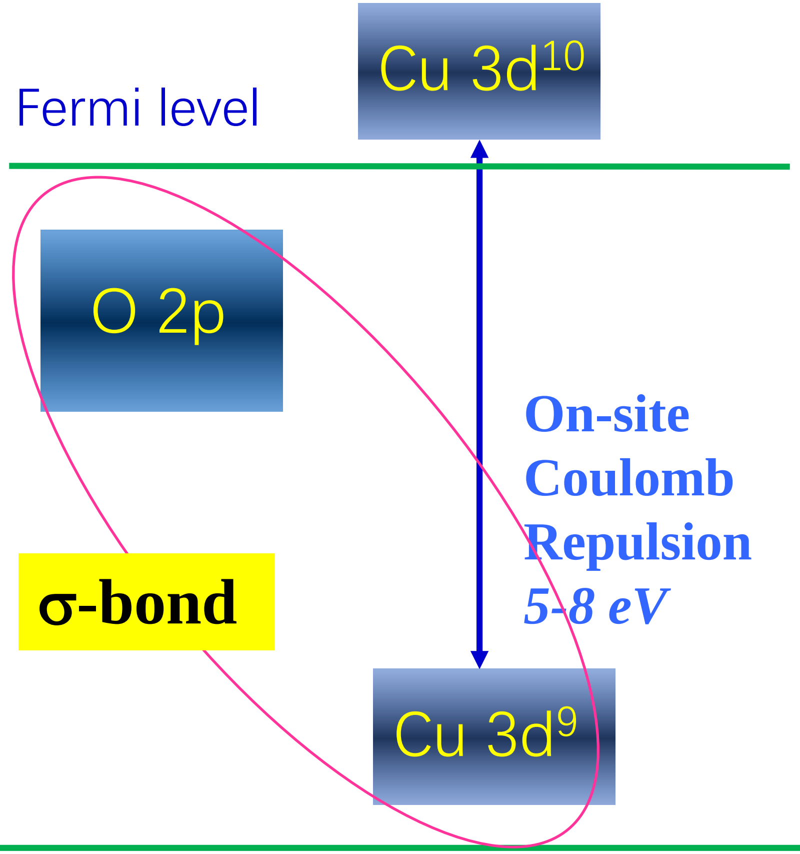
Metallizing σ-electrons: Cuprates



Cuprate SC



Cu 3d(x^2-y^2) and O 2p form a σ-bond



Cu $3d^{10}$

Fermi level

O 2p

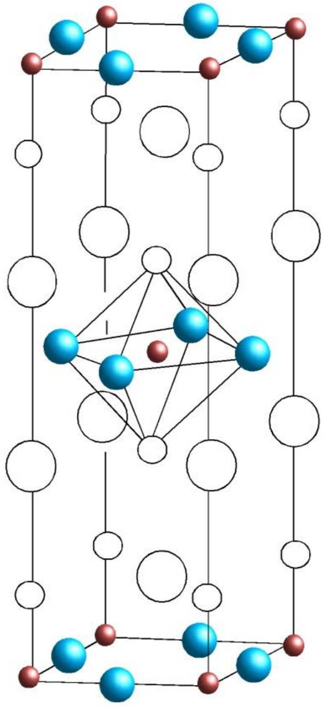
σ-bond

On-site Coulomb Repulsion ***5-8 eV***

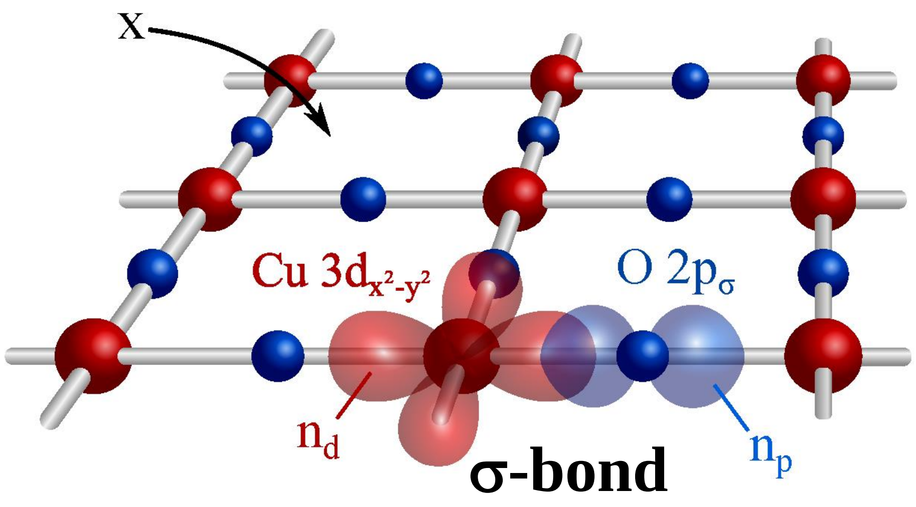
Cu $3d^9$

Hole doping lifts the Cu-O σ-bonds to the Fermi level, leading to high-Tc SC

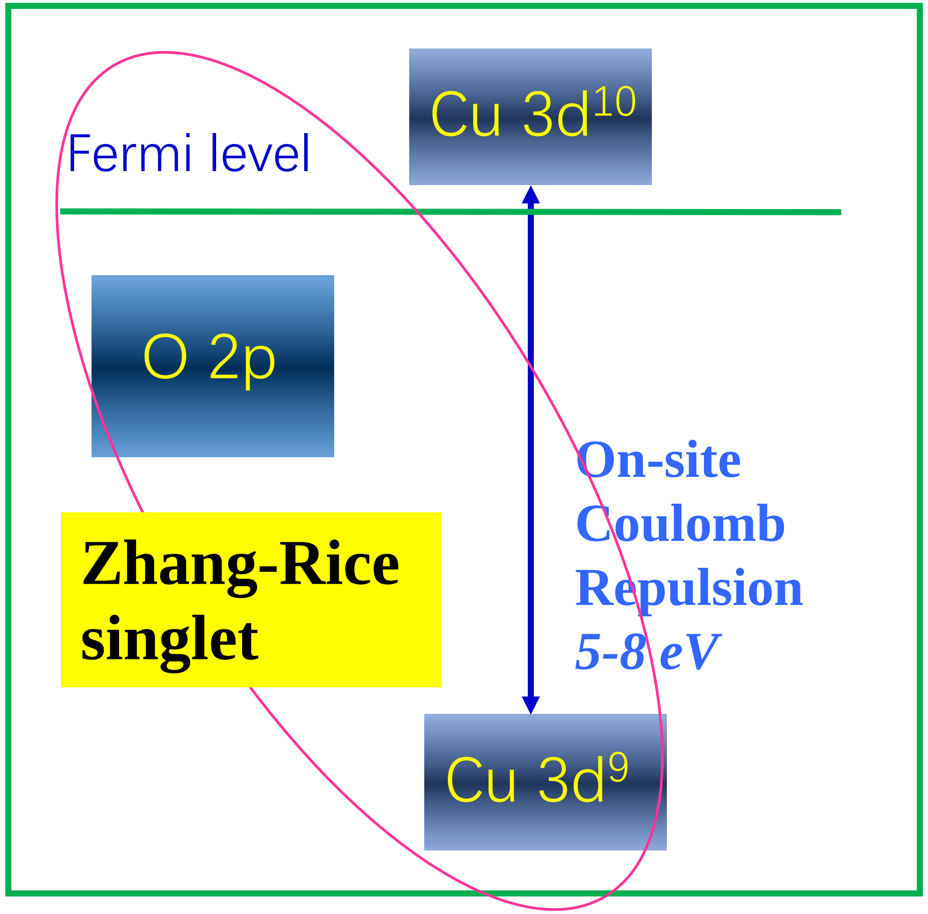
Metallizing σ-electrons: Hole Doping



Cuprate SC



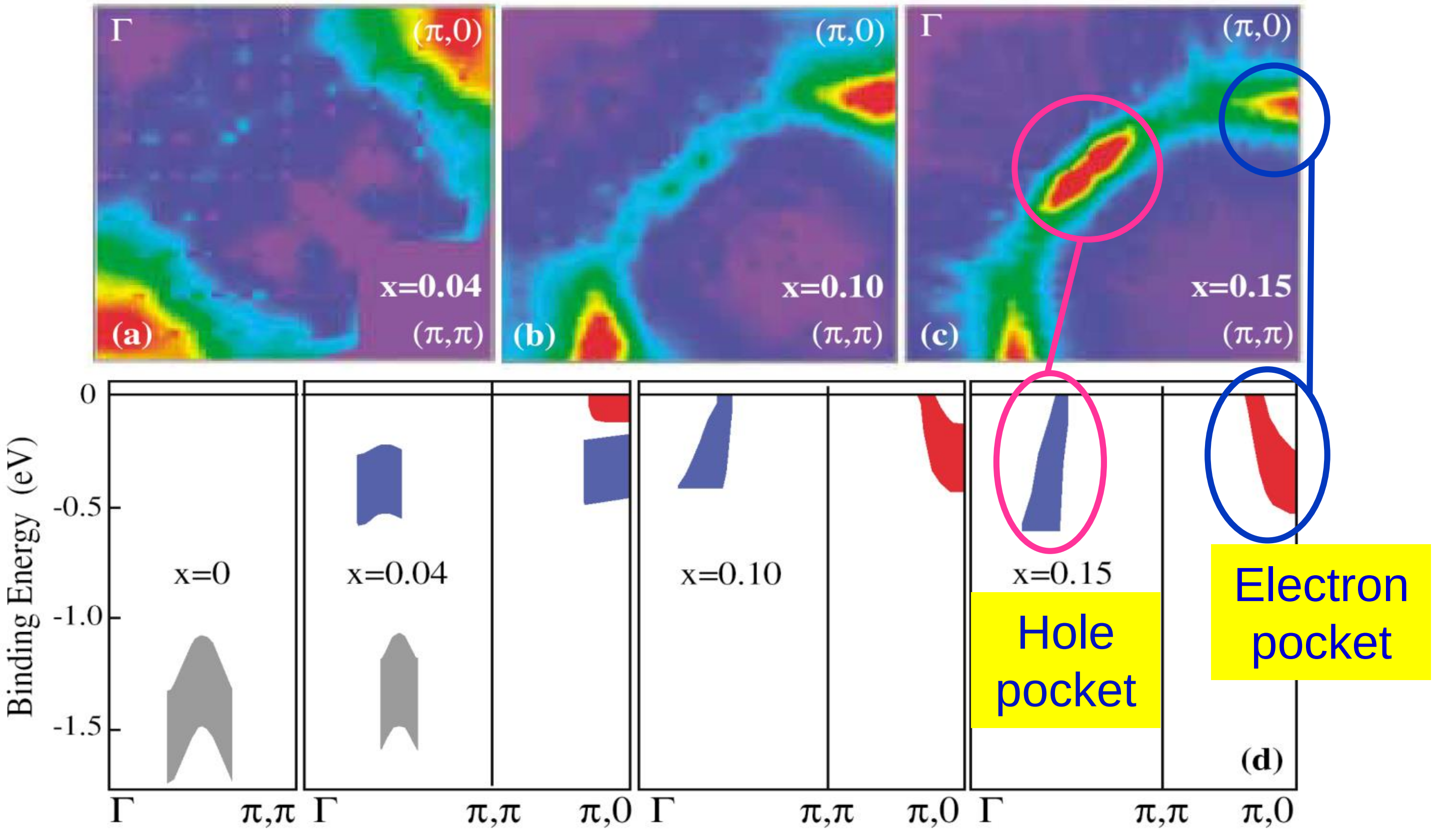
Cu 3d(x^2-y^2) and O 2p hole form a metallized Zhang-Rice singlet



Roles of antiferromagnetic fluctuations

- ✓ **release the lattice instability induced by doping**
- ✓ **enforce the metallization**

Experimental Evidence of Metallized σ-electrons

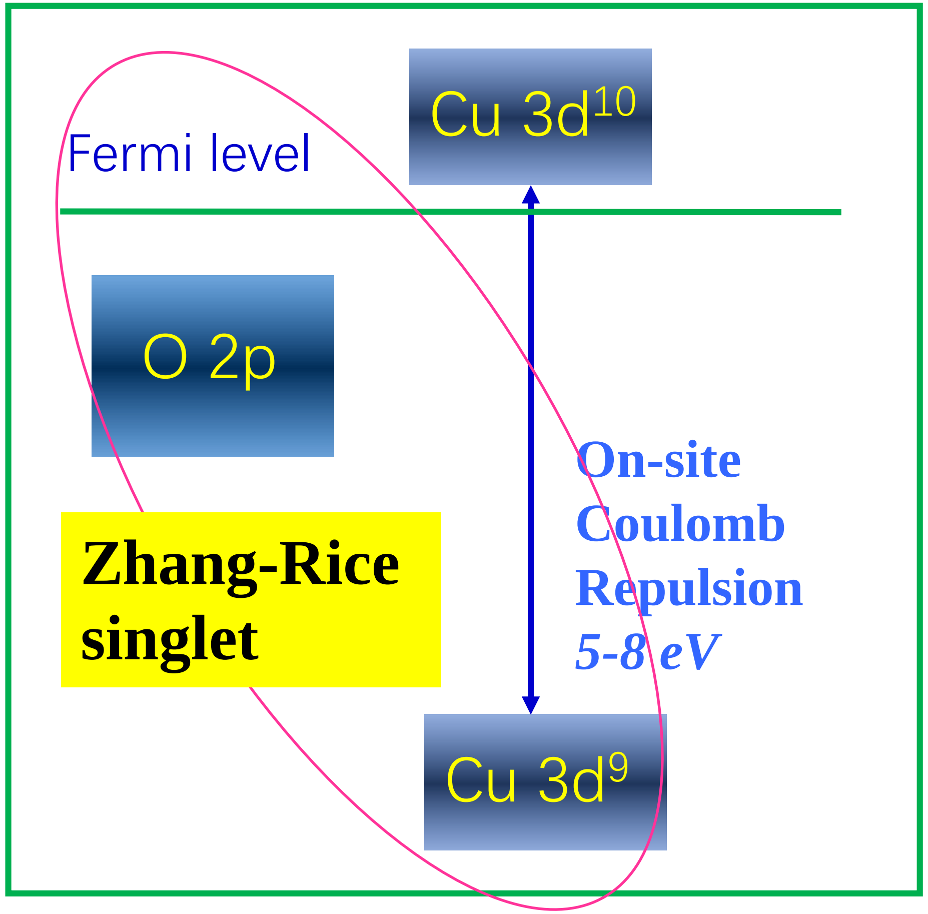


Hole pocket

Electron pocket

$Nd_{2-x}Ce_xCuO_4$

Armitage et al., PRL 88, 257001 (2002)



Cu $3d^{10}$

Fermi level

O 2p

Zhang-Rice singlet

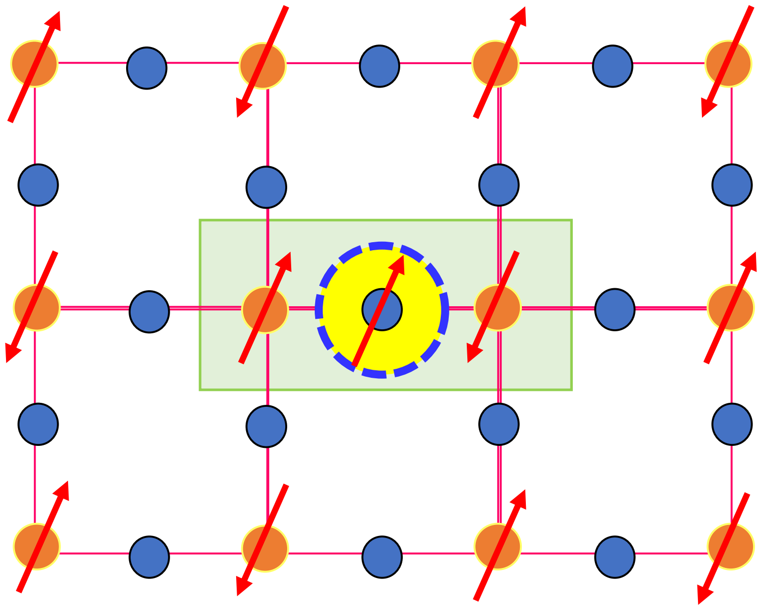
On-site Coulomb Repulsion *5-8 eV*

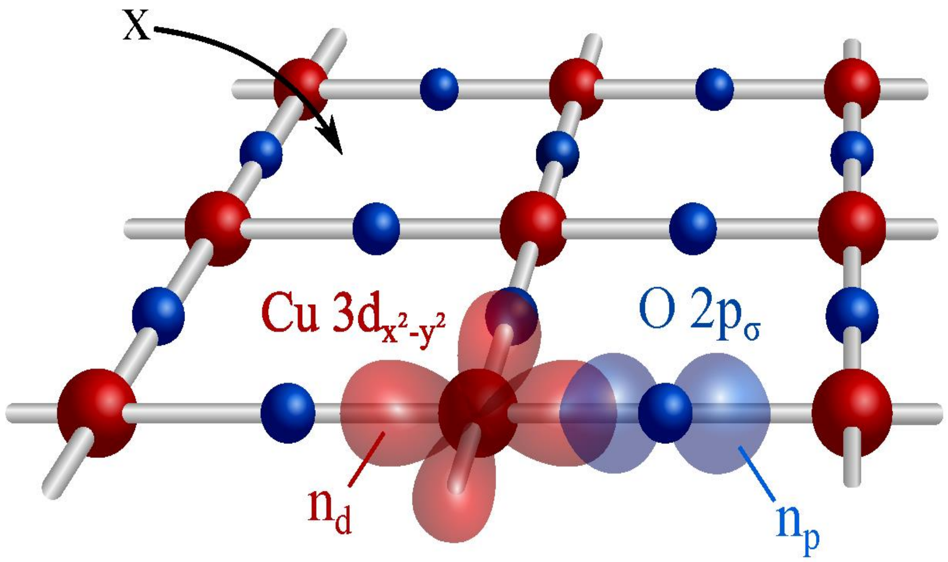
Cu $3d^9$

Role of Cu-Spin Antiferromagntic Fluctuations

Both the Cu-O σ-bonding electrons and Cu-Cu spins are coupled by the Heisenberg interaction

$$H = JS_i \cdot S_j$$

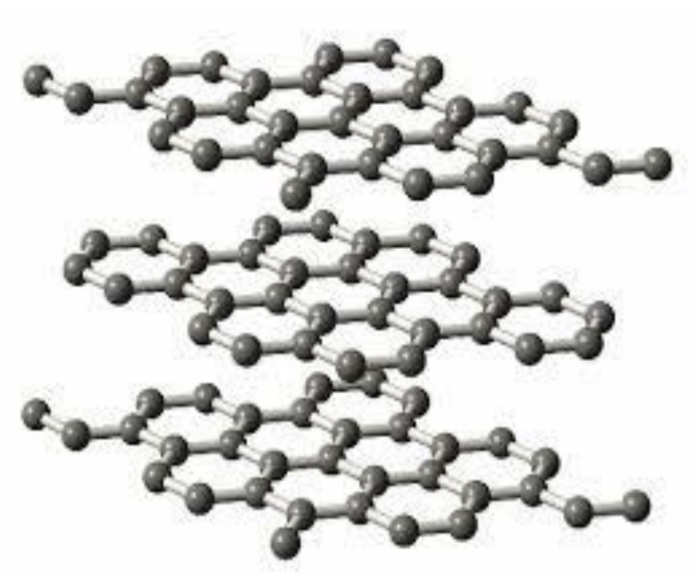


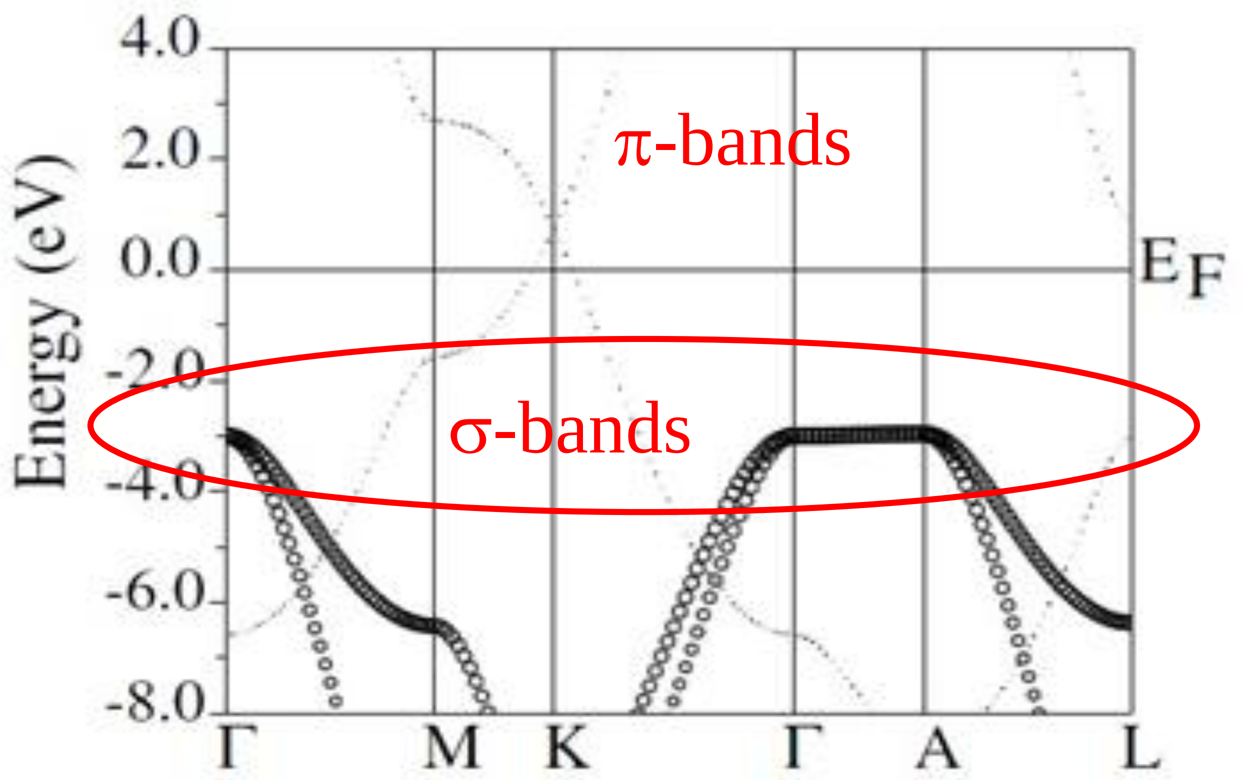


Cu-Cu spin antiferromagnetic fluctuations break the bonds and favor the metallization of σ-electrons

Metallizing σ-electrons: MgB_2

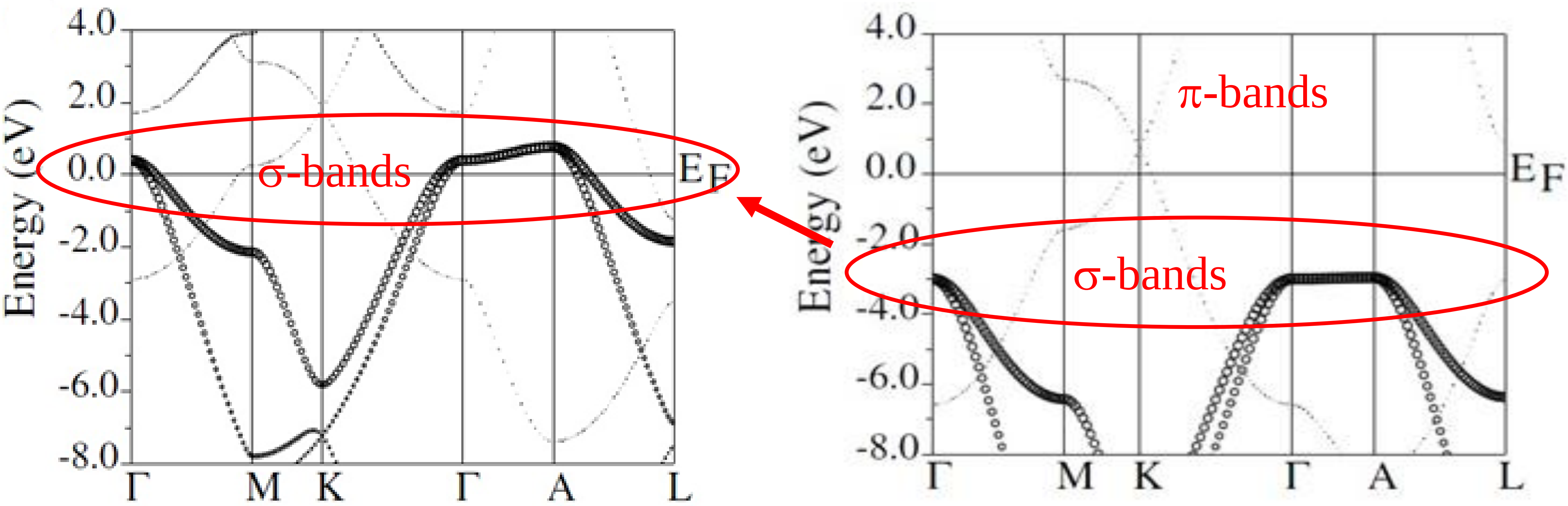
graphite



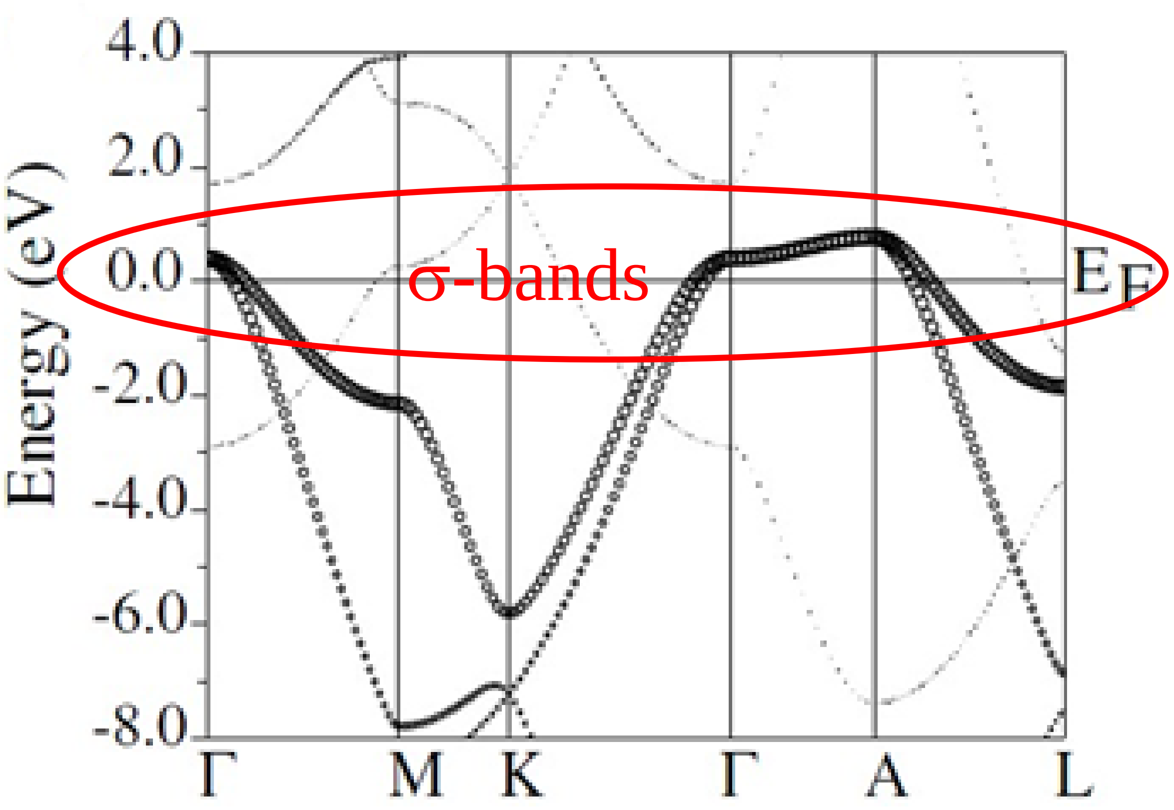


σ-band is located below the Fermi level, no contribution to conductivity

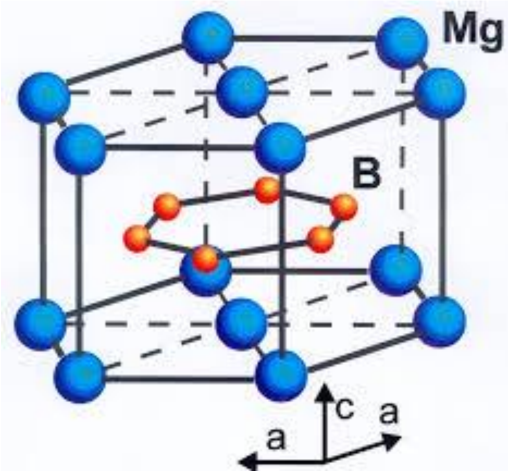
Can We Lift σ-electrons to the Fermi Level?



Can We Lift σ-electrons to the Fermi Level?



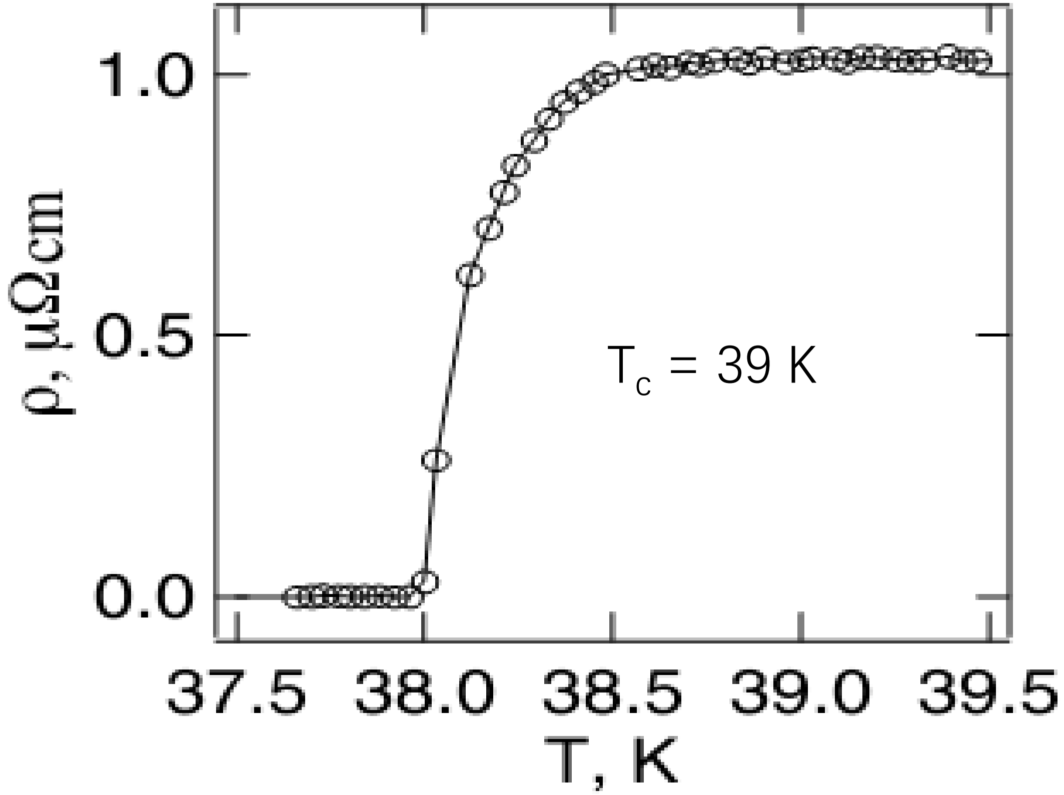
JM An & WE Pickett, PRL 86, 4366 (2001)



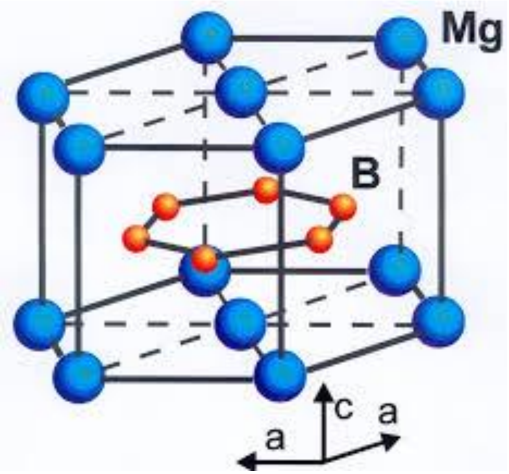
MgB_2

Mg^{2+} couples stronger with the 2p π-electrons and the 2p σ-electrons, which lowers the Fermi level of π-bands --- effectively lifting the σ-bands

Can We Lift σ-electrons to the Fermi Level?



J. Nagamatsu *et al.*, Nature 410, 63 (2001)



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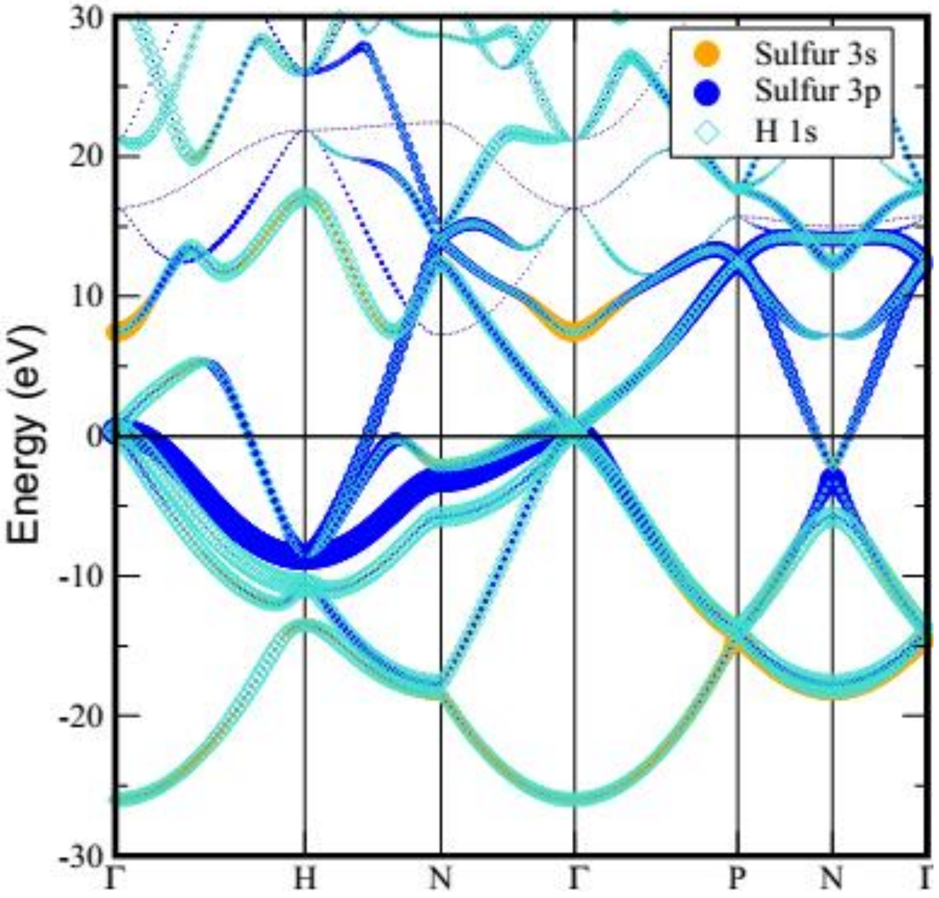
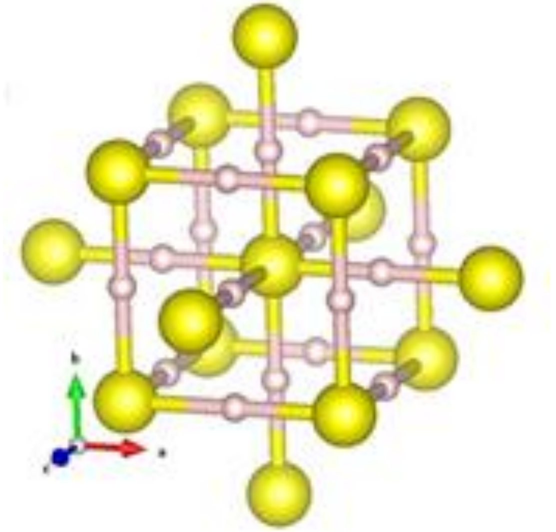
Metallizing σ-electrons: H-enriched Materials



“H_3S has a record high Tc due to its covalent bonds driven metallic”



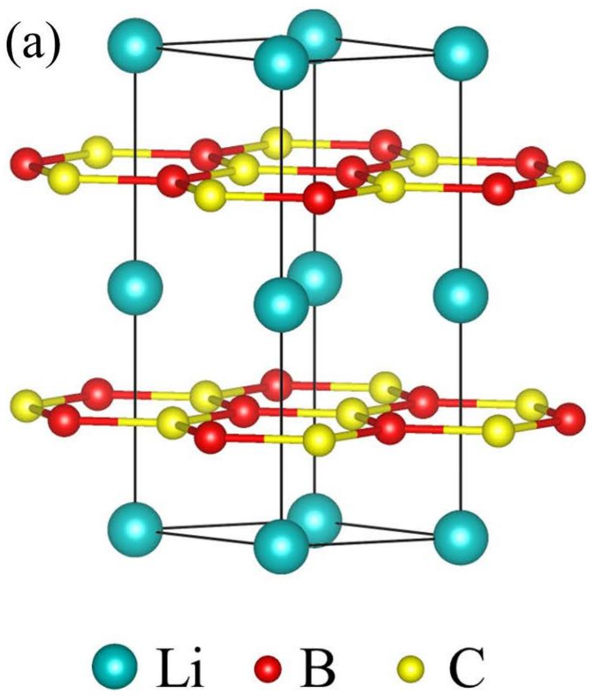
H_3S

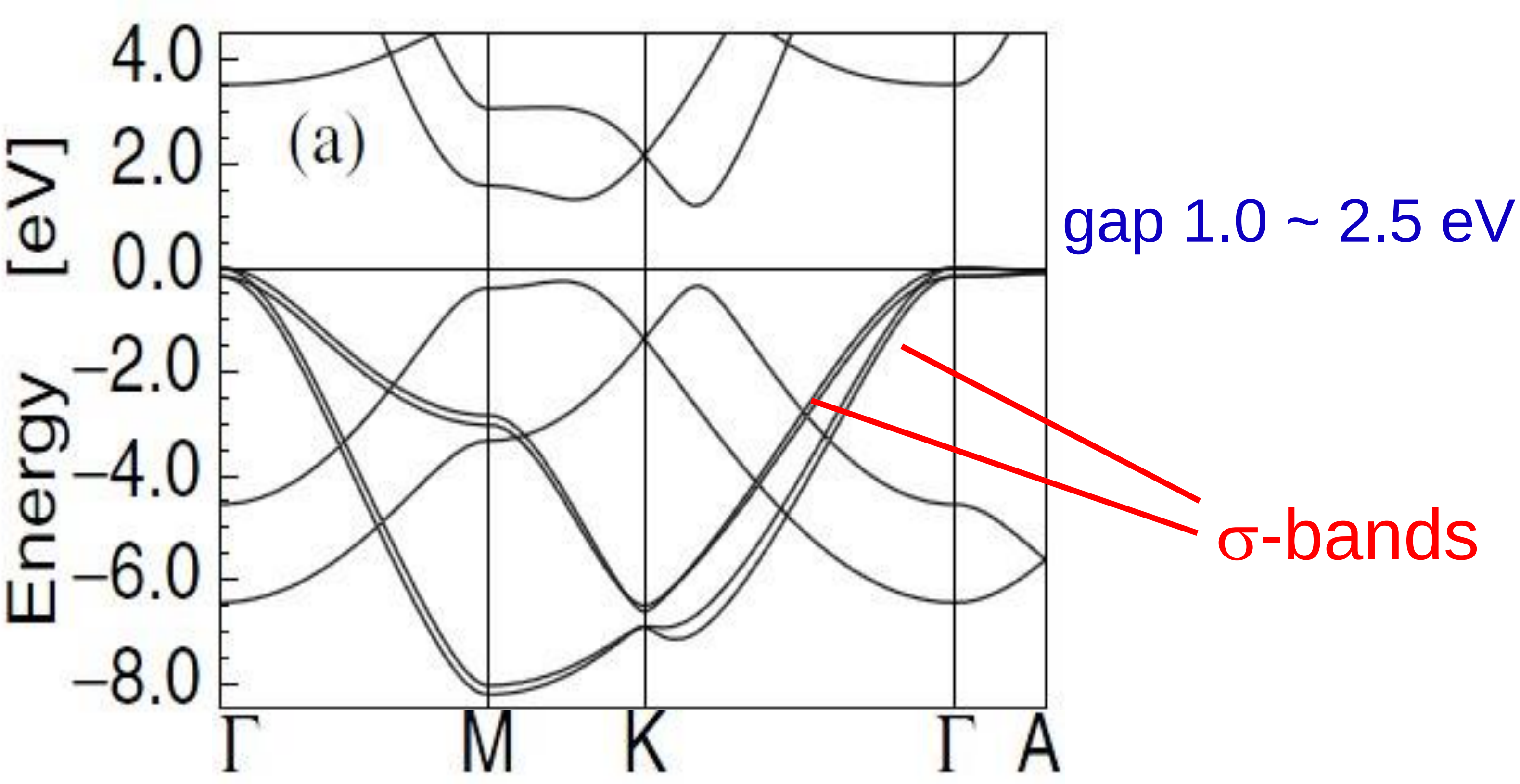
N. Bernstein, CS Hellberg, MD Johannes, II Mazin, MJ Mehl, PRB 91, 060511(R) (2015)

Theoretical predictions for a number of candidates of high-Tc superconductors

1. Hole doped LiBC

LiBC





gap 1.0 ~ 2.5 eV

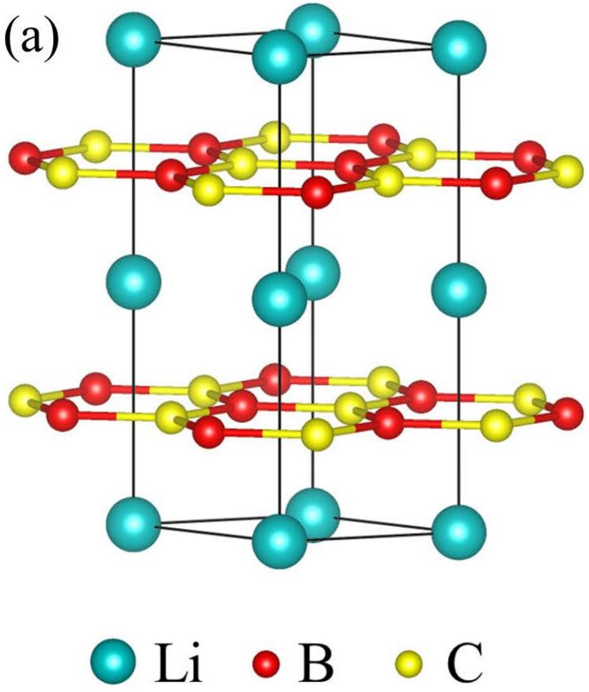
σ-bands

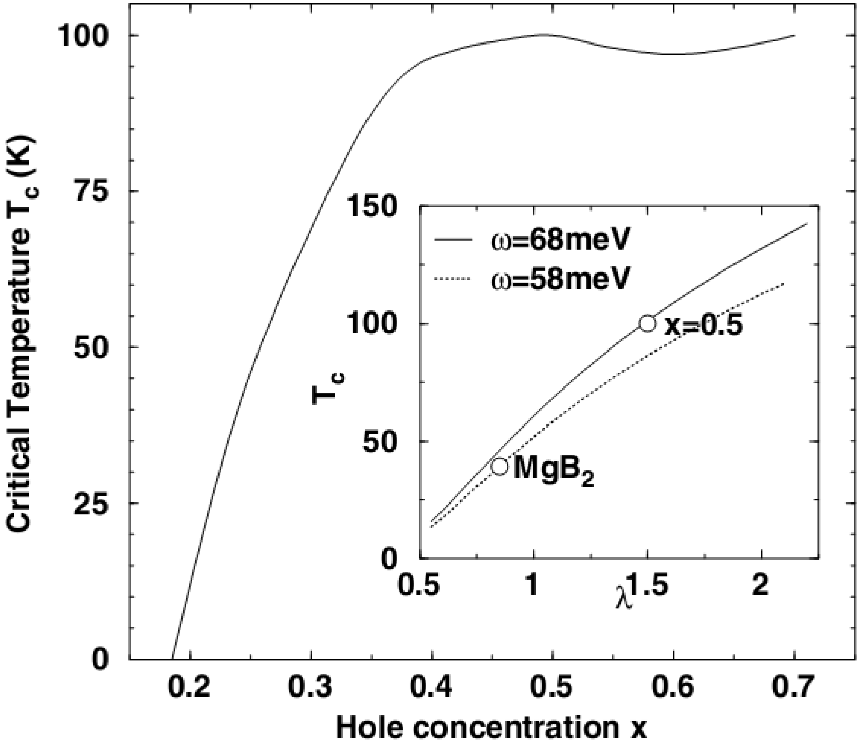
LiBC: σ-electrons are on the top valence bands

JM An & WE Pickett, PRL 86, 4366 (2001)

Predicted Tc

$Li_{0.5}BC$





$Li_{0.5}BC$:

$\lambda = 1.5$

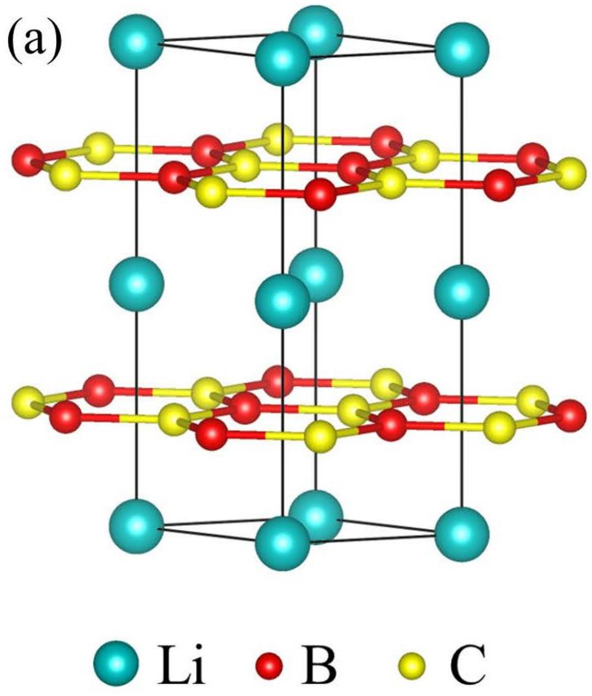
$\mu^* = 0.09$

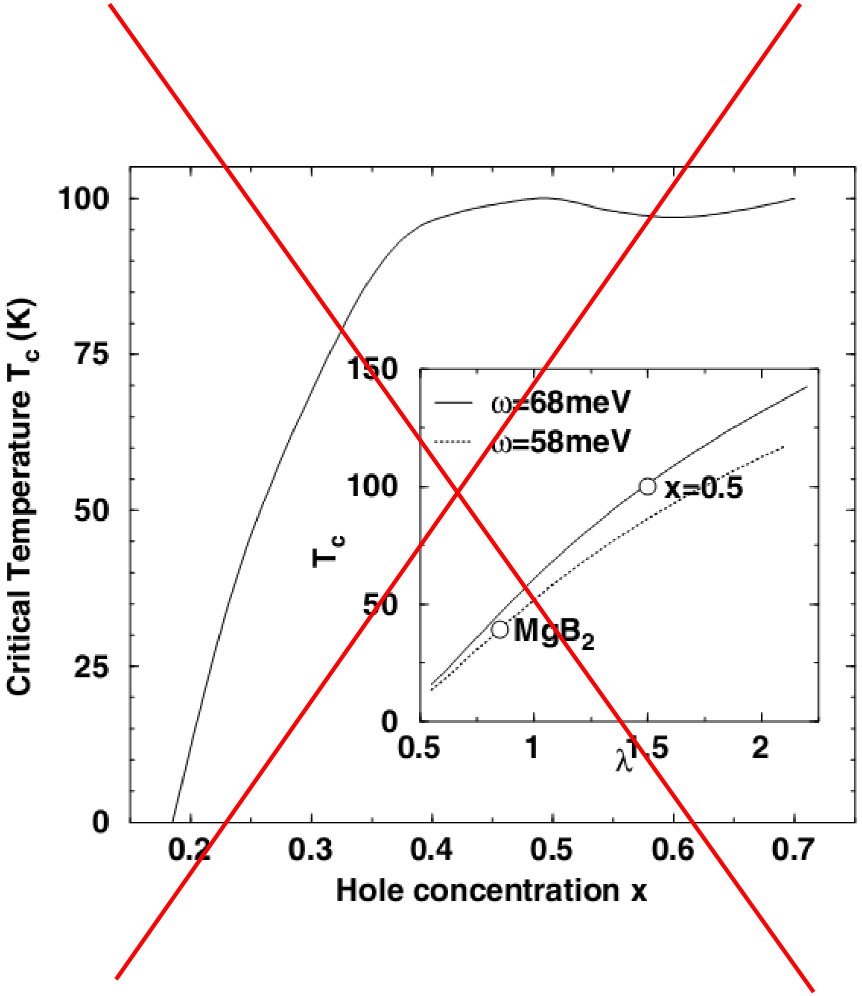
$T_c = 100$ K

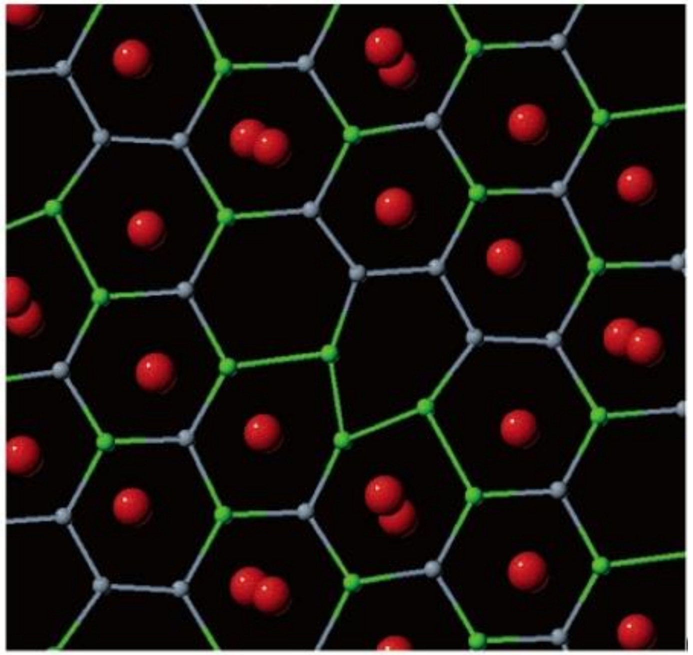
JM An & WE Pickett, PRL 86, 4366 (2001)

Li deficiency Distorts LiBC

$Li_{0.5}BC$



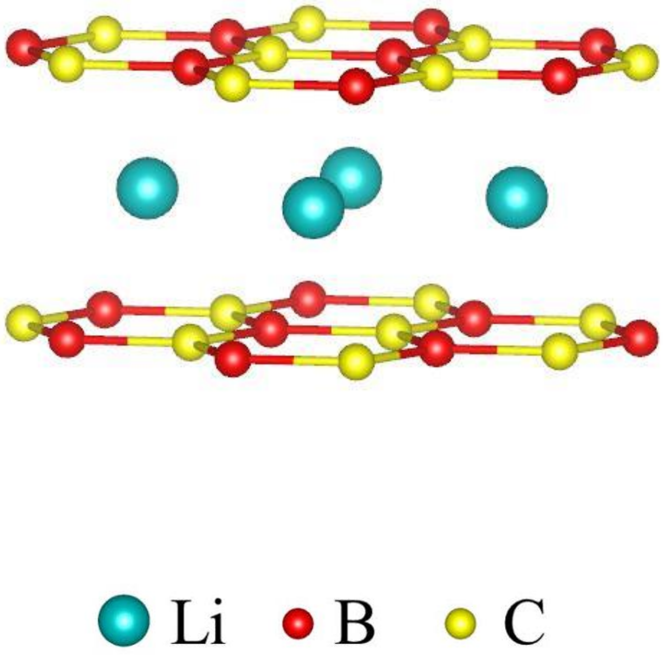


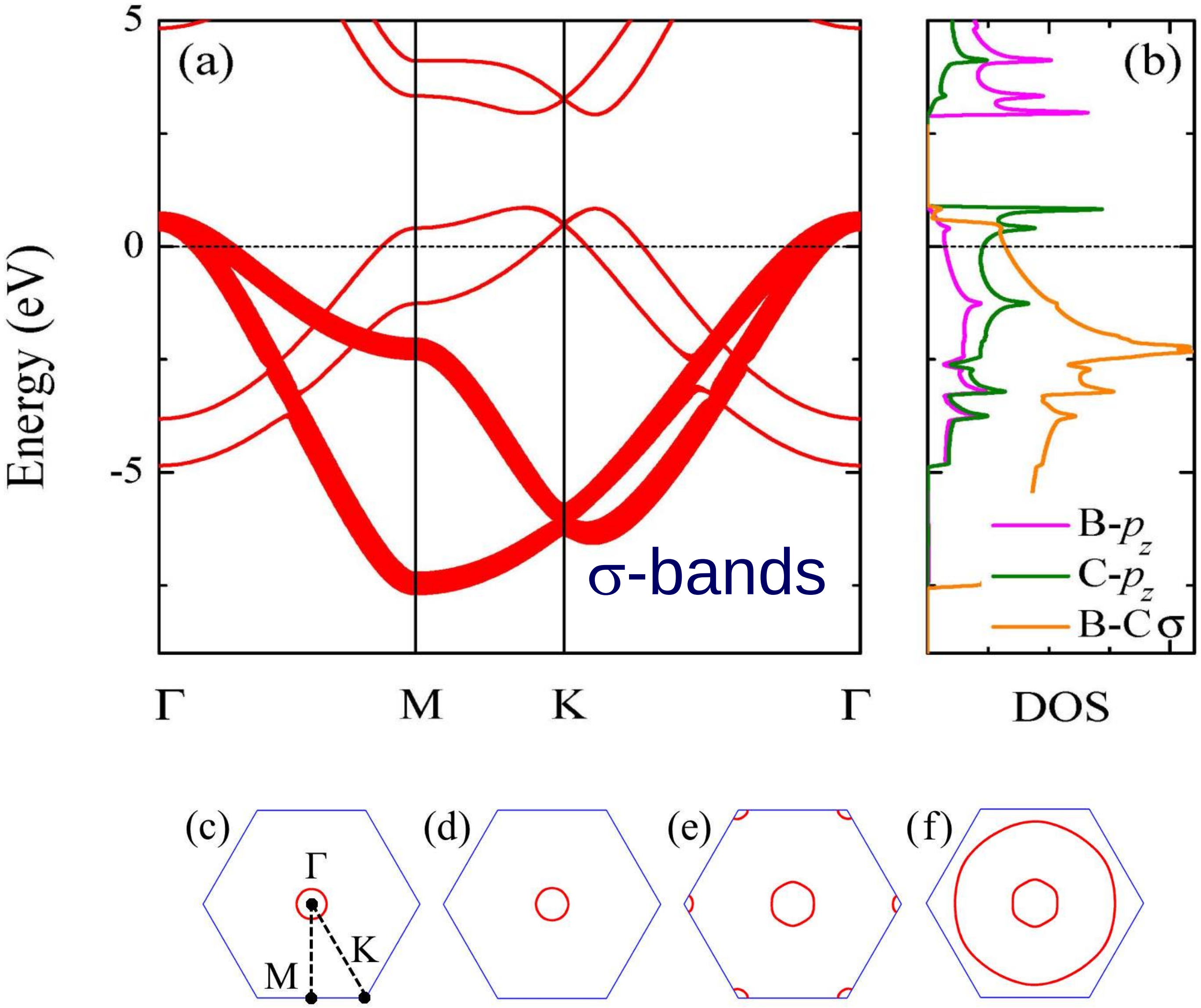


AM Fogg *et al.*, JACS 128, 10043 (2006)

Can We Dope LiBC without Introducing Li Deficiency?

Trilayer LiB_2C_2

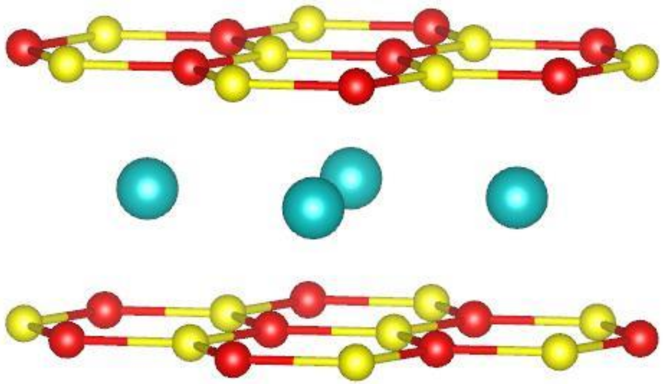


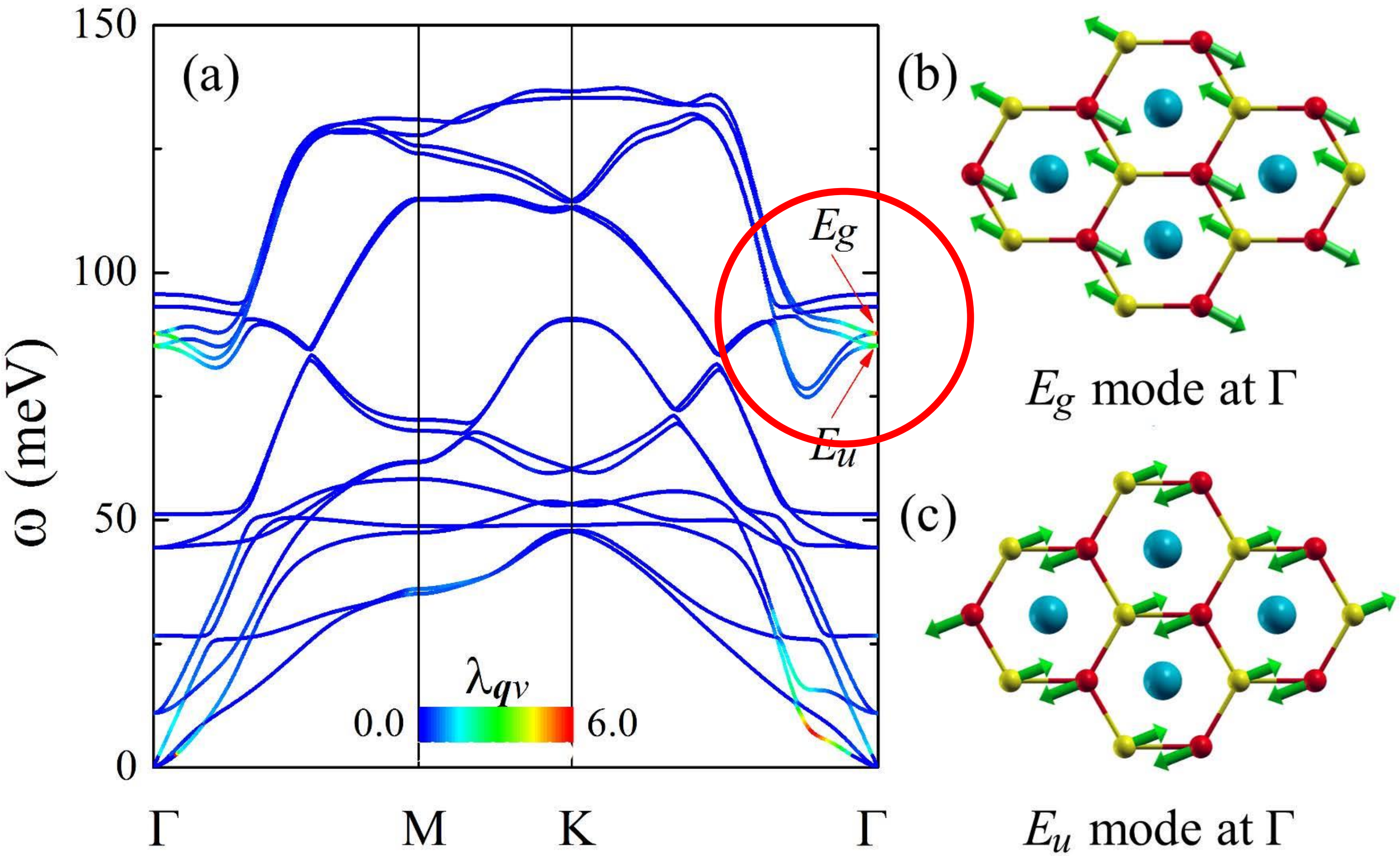


Gao, Yan, Lu, Xiang, arXiv:1911.12690

Trilayer LiB_2C_2 is structurally stable

Trilayer LiB_2C_2



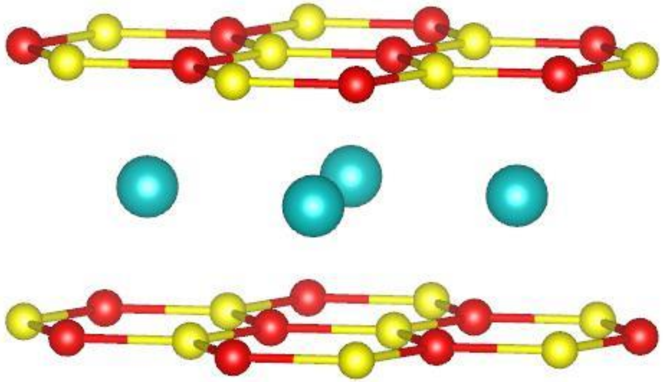


Gao, Yan, Lu, Xiang, arXiv:[1911.12690]

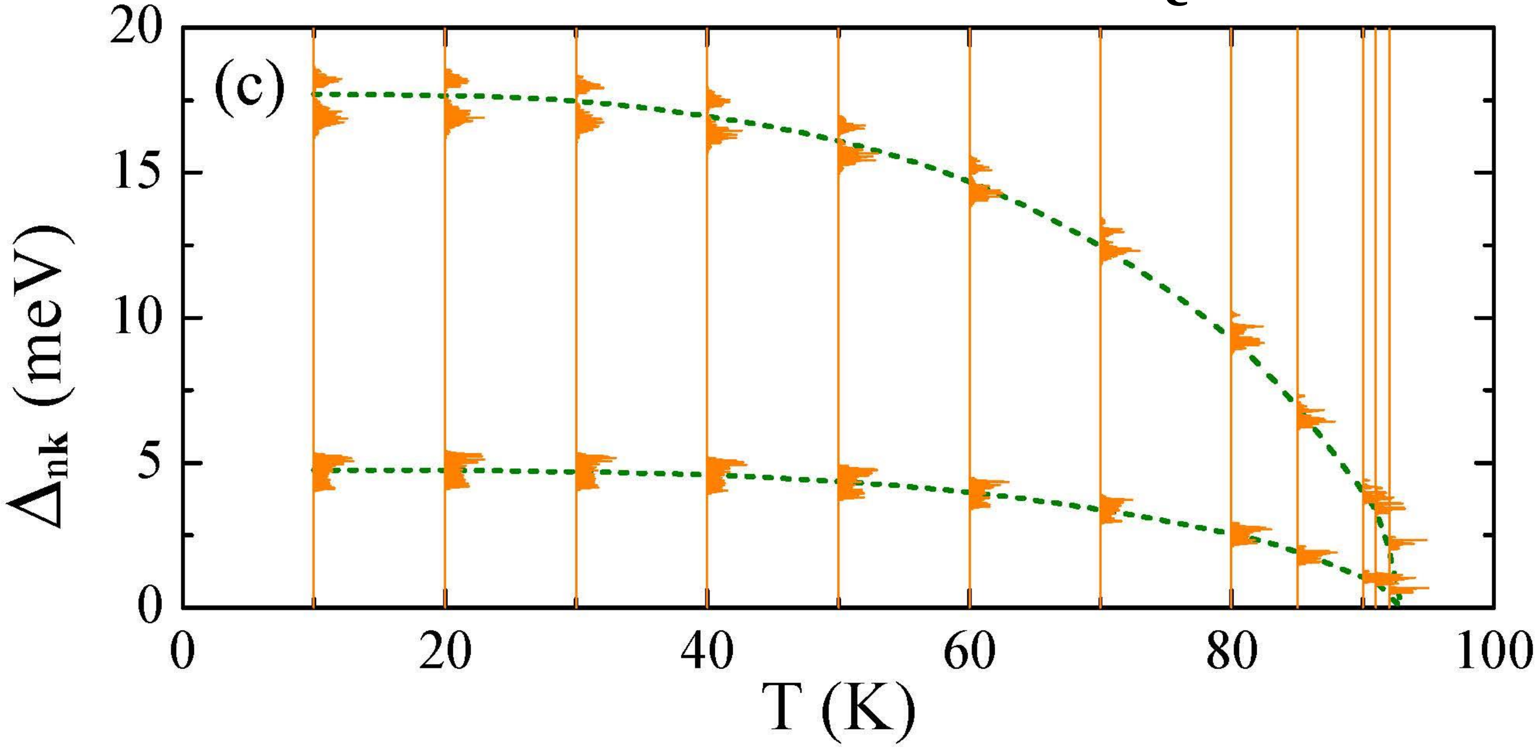
No imaginary frequency in the spectrum

Trilayer LiB_2C_2 is a Good High-Tc Candidate

Trilayer LiB_2C_2



T_c ~ 92 K

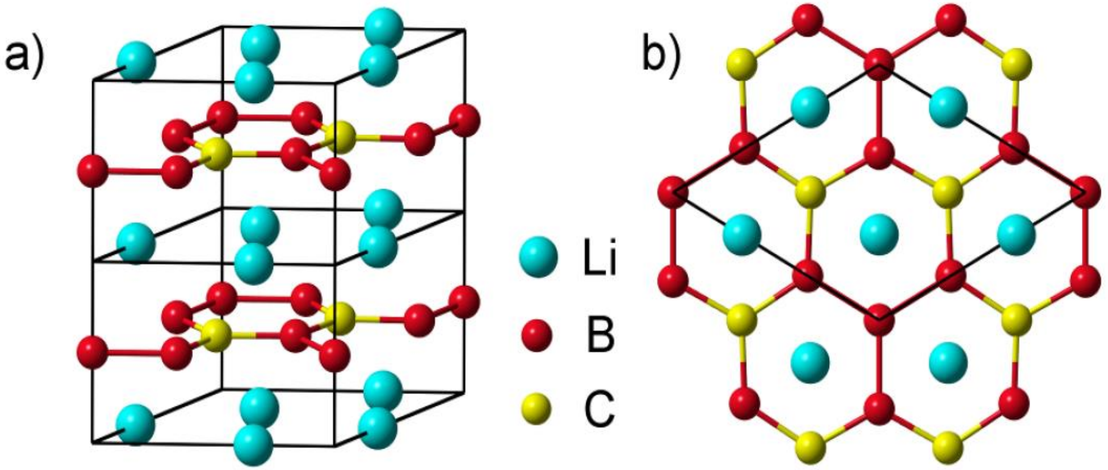


Superconducting energy gap as a function of temperature

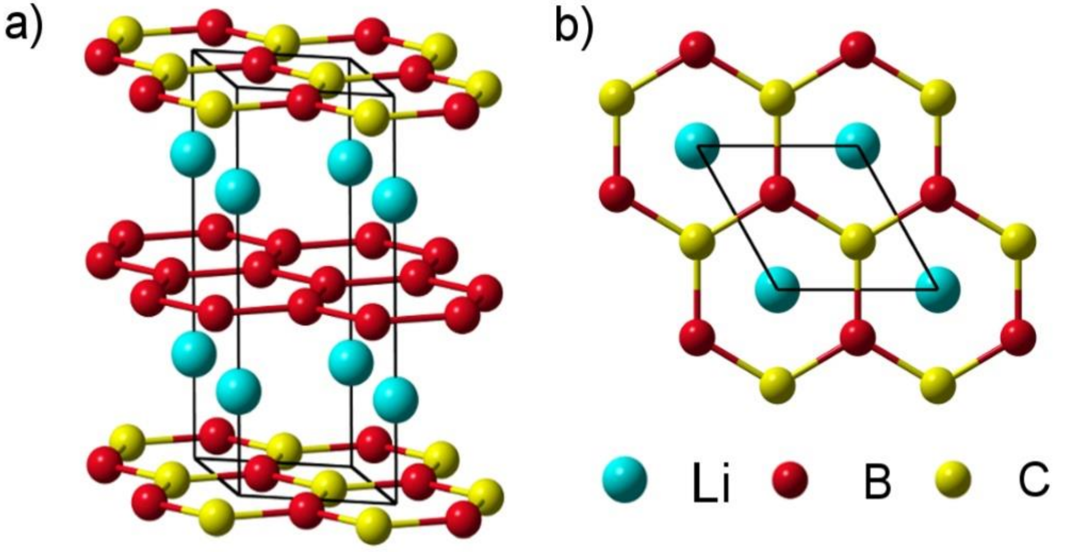
Obtained by solving Eliasberg equation

Gao, Yan, Lu, Xiang, arXiv:1911.12690

Hole doped LiBC: More suggestions



$Li_3B_4C_2$: T_c ~ 50 K

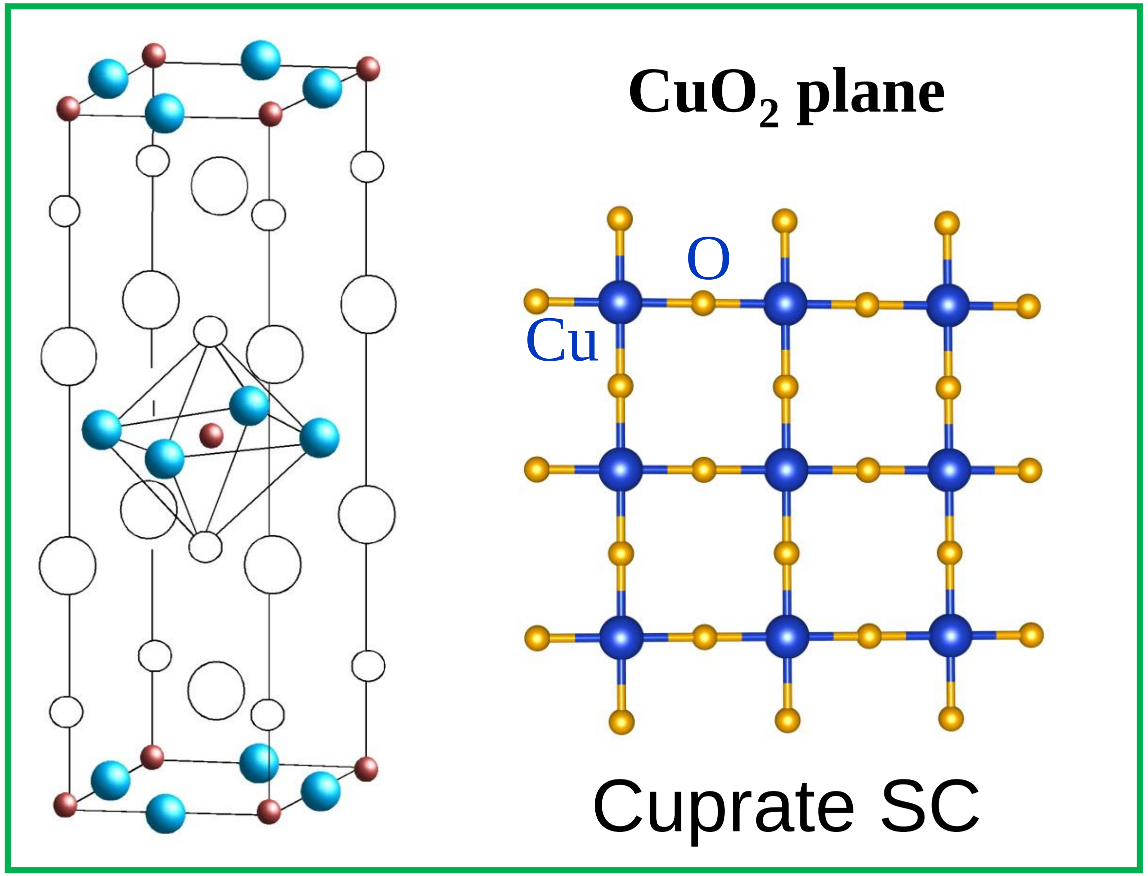


Li_2B_3C: T_c ~ 55 K

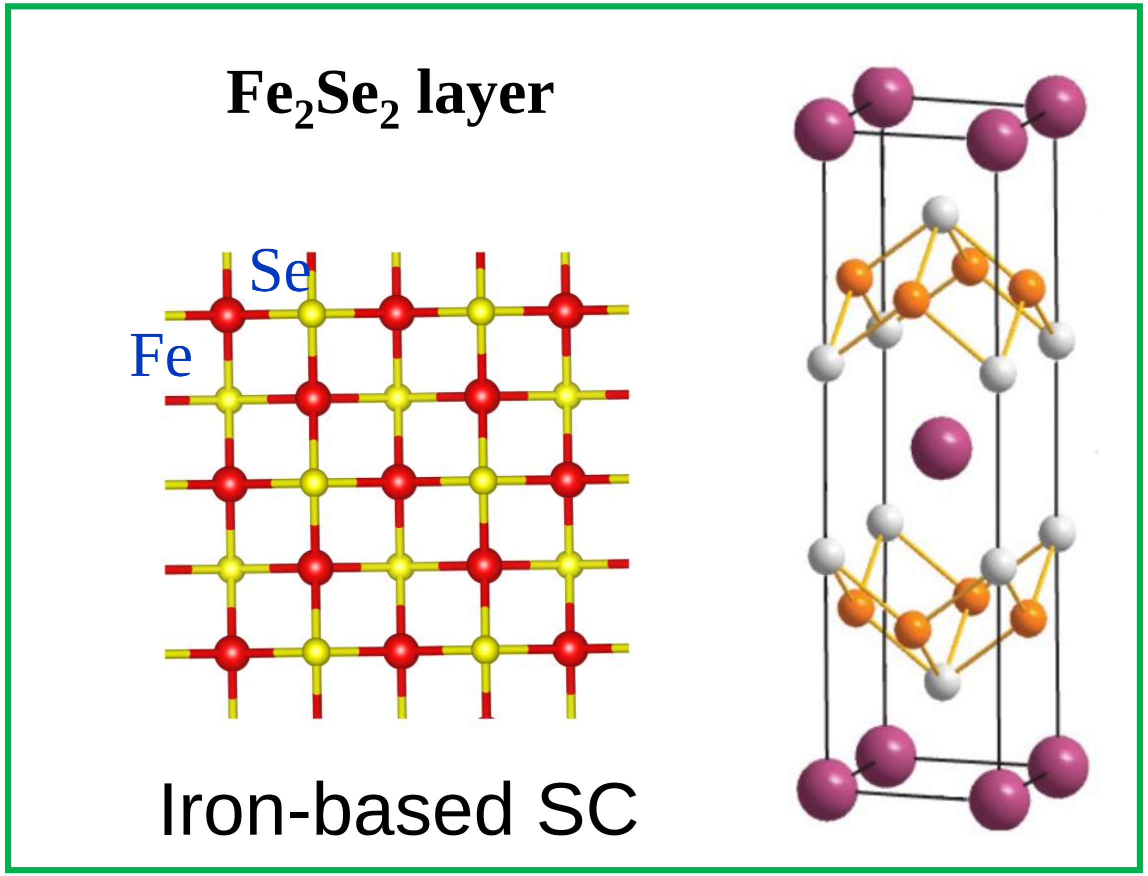
$Li_3B_4C_2$ and Li_2B_3C: dope holes without introducing lattice distortions

M Gao, ZY Lu, T Xiang, PRB 91, 045132 (2015)

2. Materials analog to the cuprates


CuO_2 plane

Cuprate SC


Fe_2Se_2 layer

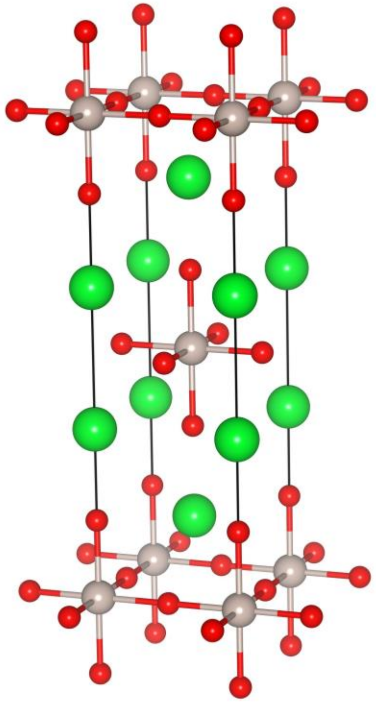
Iron-based SC

There is high chance to find metallized σ-bonding electrons in materials isostructural and isoelectronic to cuprate superconductors

They may become high-Tc SC by doping

Superconducting materials isostructural to cuprates

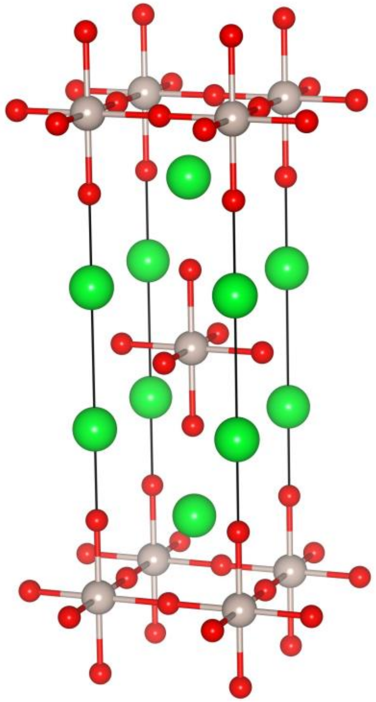
Sr_2RuO_4



T_c ~ 2 K

Maeno et al., Nature (1994)

Sr_2IrO_4

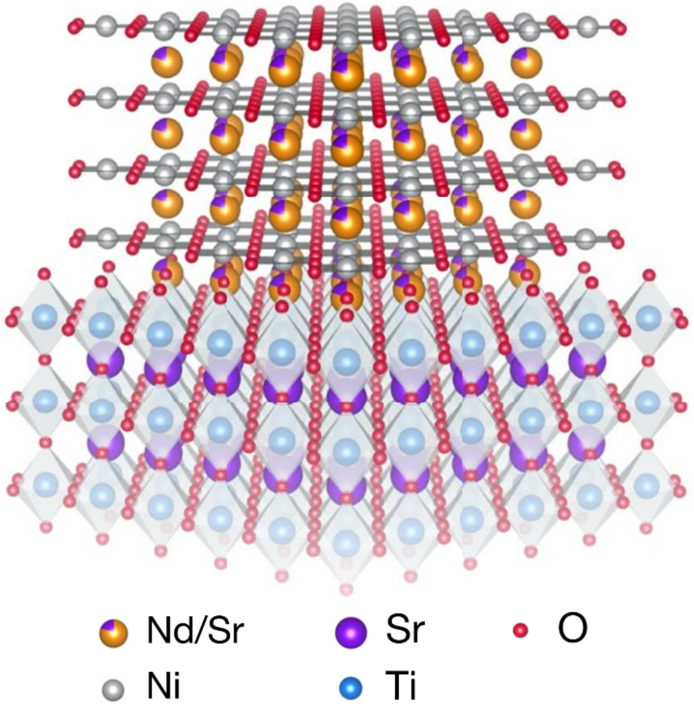


T_c ~ 50 K ?

STM, no transport

Kim et al, PRL (2012)

$Nd_{0.8}Sr_{0.2}NiO_2$

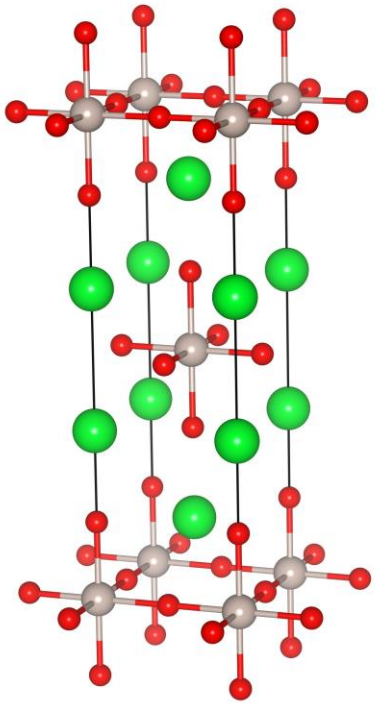


T_c ~ 9 - 15 K

Li et al., Nature (2019)

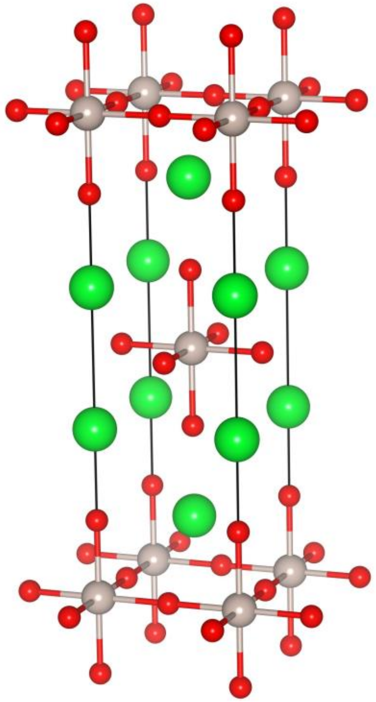
Are they electronically similar to cuprates?

Sr_2RuO_4 ✕



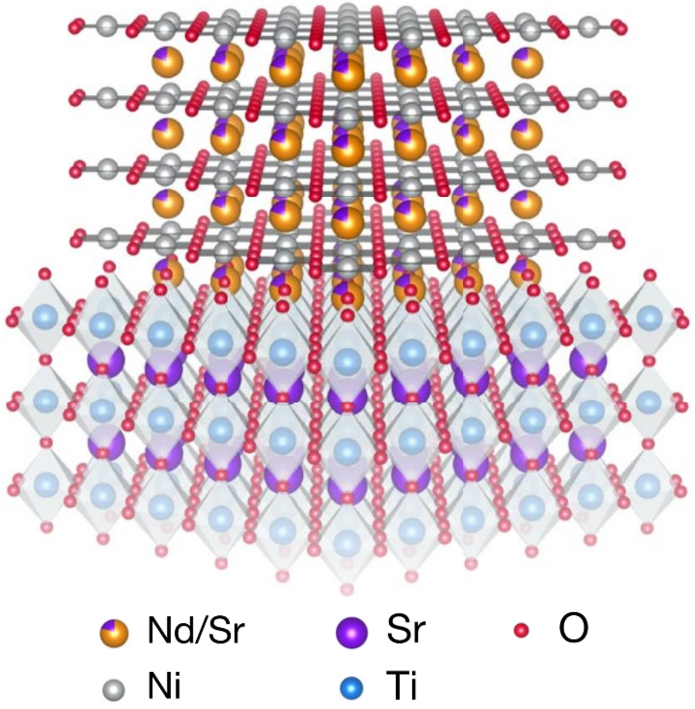
- ✓ weak bonding
- ✓ weak AFM fluctuation

Sr_2IrO_4 √



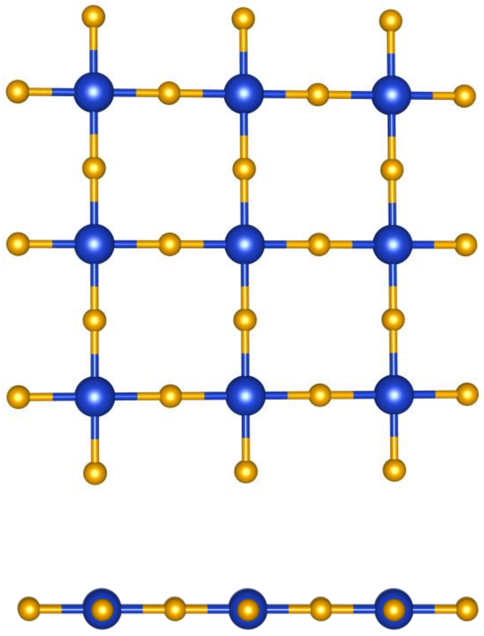
- ✓ spin-orbital coupling
- ✓ AFM fluctuation
- ✓ surface doping only

$Nd_{0.8}Sr_{0.2}NiO_2$?

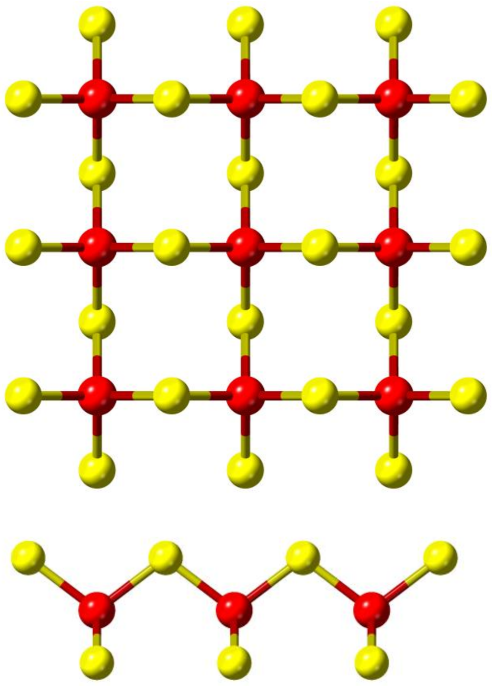


- ✓ 3d-4f hybridized
- ✓ weak AFM fluctuation
- ✓ weak Ni 3d-O 2p bond

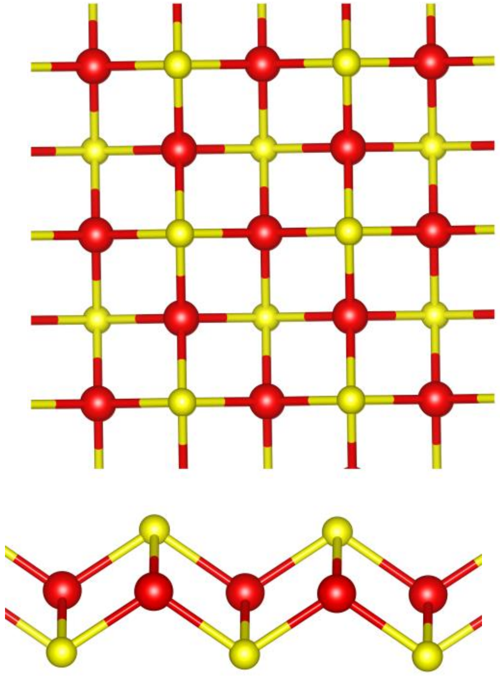
Can we find a Fe-based analog of the cuprate?



CuO_2 plane



$FeSe_2$ layer



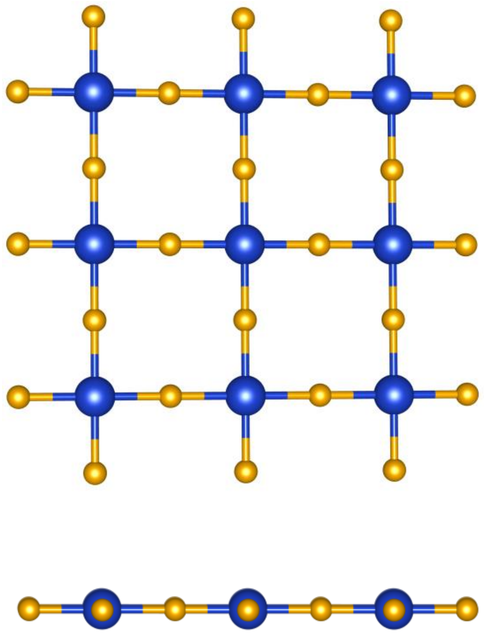
Fe_2Se_2 layer

Zhao, Ma, Lu, Xiang, arXiv:1910.03545

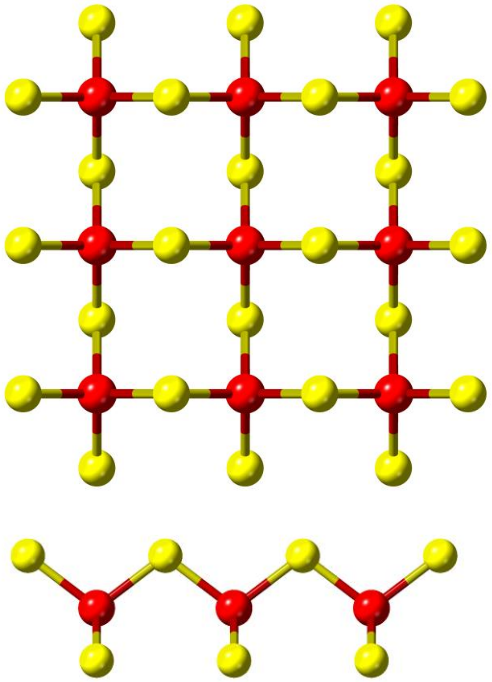
$AFeSe_2$: Fe-based superconducting analogs of the cuprates,

This kind of material exists: $AFeSe_2$ (A=Tl, K, Rb, Cs)

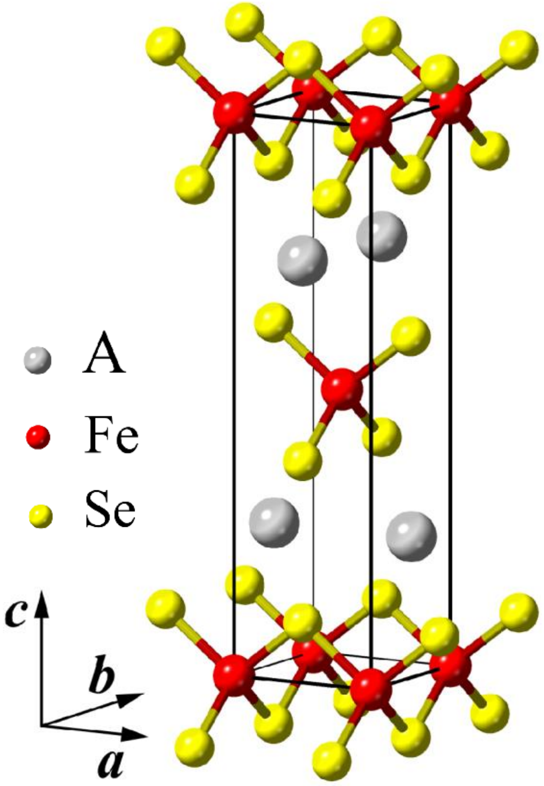
CuO_2 plane



$FeSe_2$ layer



$AFeSe_2$ (A=Tl, K, Rb, Cs)



I-4m2 symmetry Group

$TlFeSe_2$ synthesis

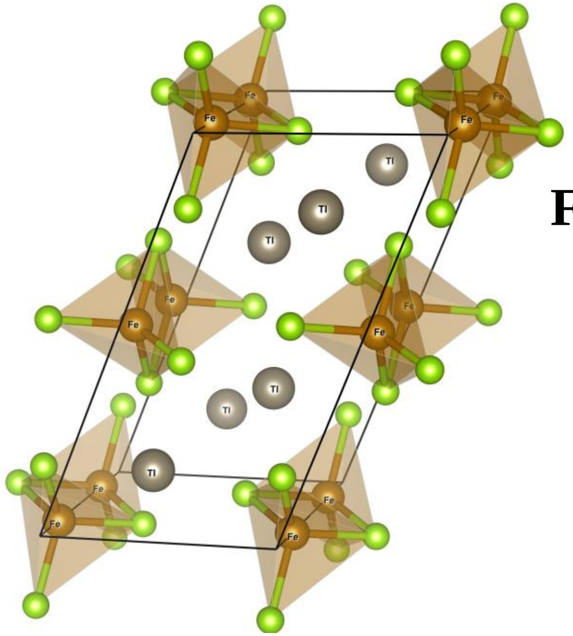
A. Kutoglu, Naturwissenschaften 61, 125 (1974)

G. D. Guseinov et al., Inorg. Mat. 27, 377 (1991)

Other Structures of $AFeSe_2$

Quasi-1D antiferromagnetic semiconductor

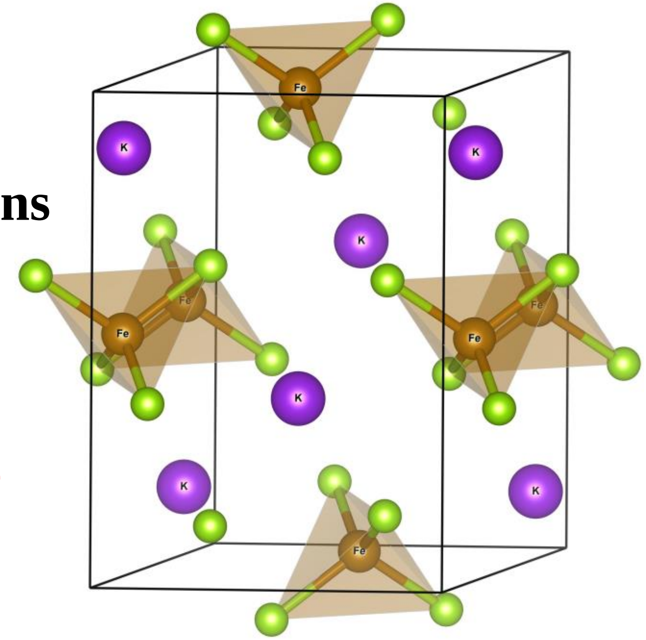
C2/m



$FeSe_4$ chains

2-3 μ_B/Fe

C2/c



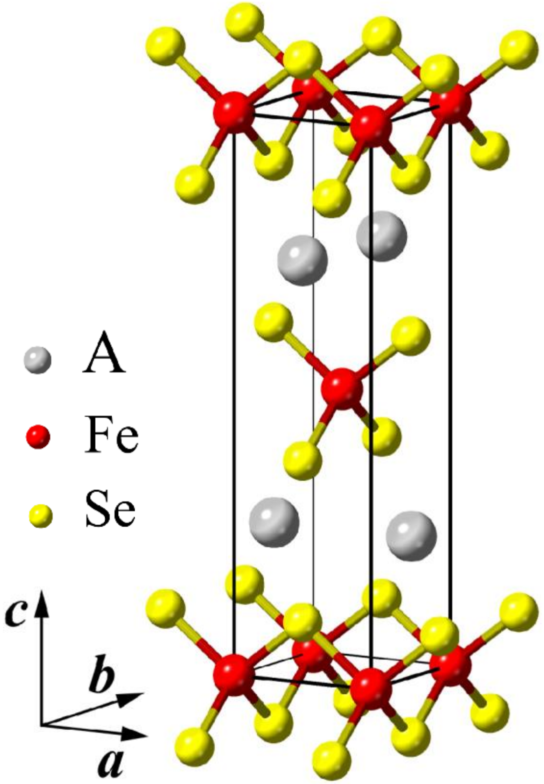
$TlFeSe_2$: Klepp and Boller, Monatshefte fur Chemie/Chemical Monthly (1979)

$CsFeSe_2$: Stuble and Rohr, Zeitschrift fr anorganische und allgemeine Chemie (2017)

$KFeSe_2$, $RbFeSe_2$

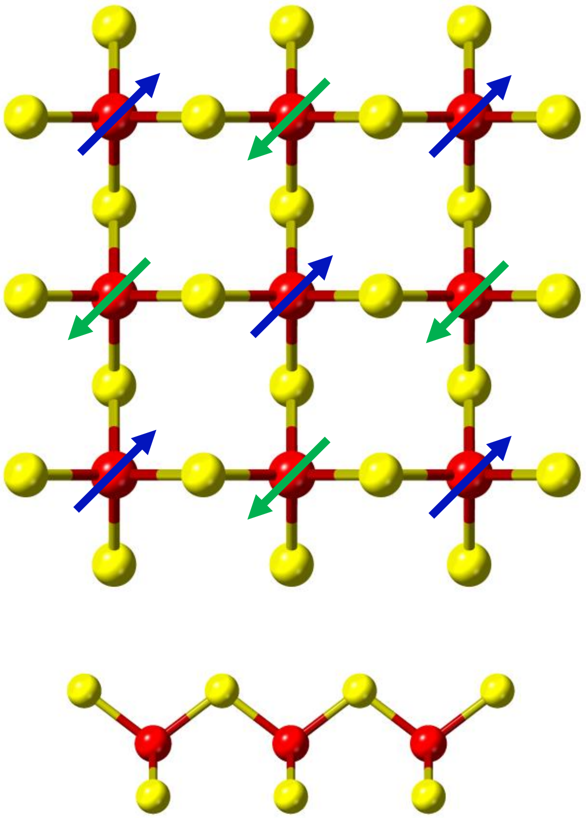
Bronger et al., J. Solid State Chem. (1987

$AFeSe_2$ (A=Tl, K, Rb, Cs)



I-4m2 symmetry Group

AFeSe$_2$ is similar to the cuprate parent compounds

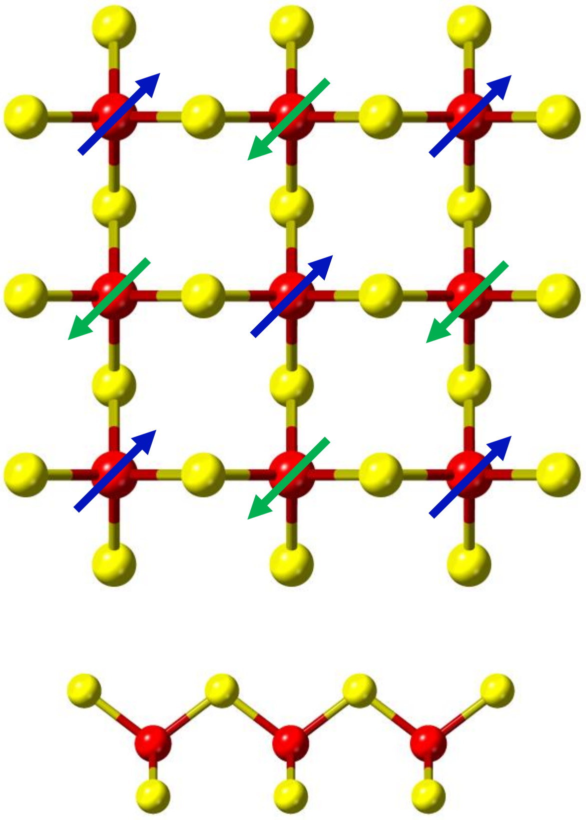

FeSe$_2$ layer

AFeSe$_2$ is an antiferromagnetic insulator
The ground state is Neel ordered

AFeSe$_2$: charge gap

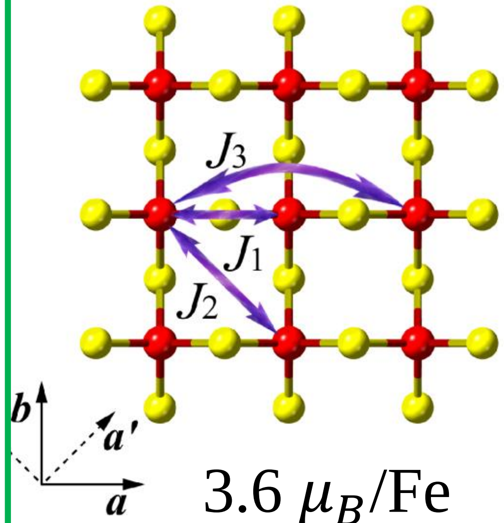
Tl, K:	**22meV**
Rb:	**56meV**
Cs:	**98meV**
Cuprate:	**2 eV**

Antiferromagnetic coupling in AFeSe$_2$



FeSe$_2$ layer

$$H = \sum_{\langle ij\rangle} \left(J_1 \delta_{\langle i,j\rangle_1} + J_2 \delta_{\langle i,j\rangle_2} + J_3 \delta_{\langle i,j\rangle_3}\right) S_i \cdot S_j$$



3.6 μ_B/Fe

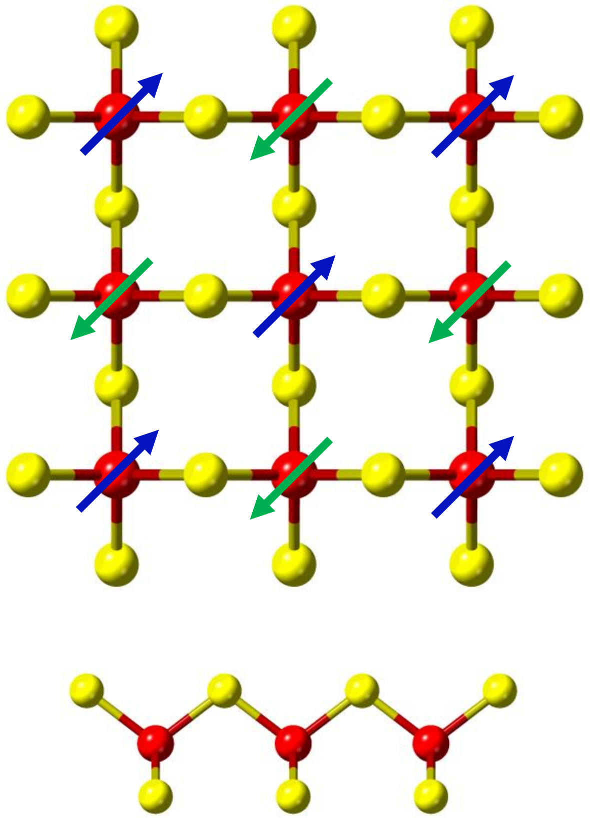
AFeSe$_2$	J$_1$	J$_2$	J$_3$
TlFeSe$_2$	115.01	9.29	10.92
KFeSe$_2$	115.00	6.04	9.29
RbFeSe$_2$	115.75	7.62	15.96
CsFeSe$_2$	115.62	8.62	14.79

meV/S^2

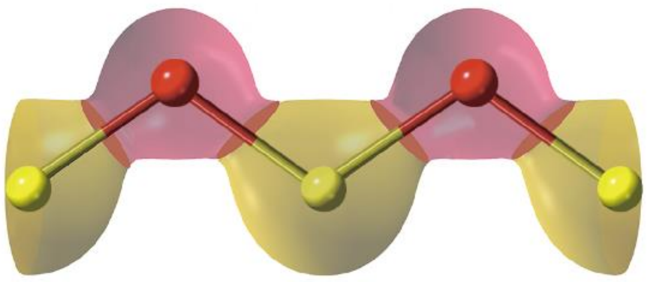
comparable to cuprates

AFeSe$_2$: Charge and Spin Density Distribution

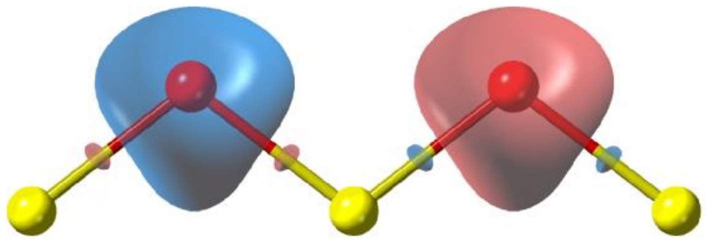
FeSe$_2$ layer



Charge density



Spin density



- Fe-Se: Strong covalent hybridized
- Fe-Fe: No direct interaction
- Magnetic interaction between Fe moments arises from Se-bridged AFM superexchange

Summary

- Metallizing strong bonding electrons provides a universal route to high-Tc superconductivity
- LiB_2C_2, Li3B4C2, Li2B3C, and doped $AFeSe_2$ (A=Tl,K,Rb,Cs) are good candidates of high-Tc SC

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Renmin Univ China

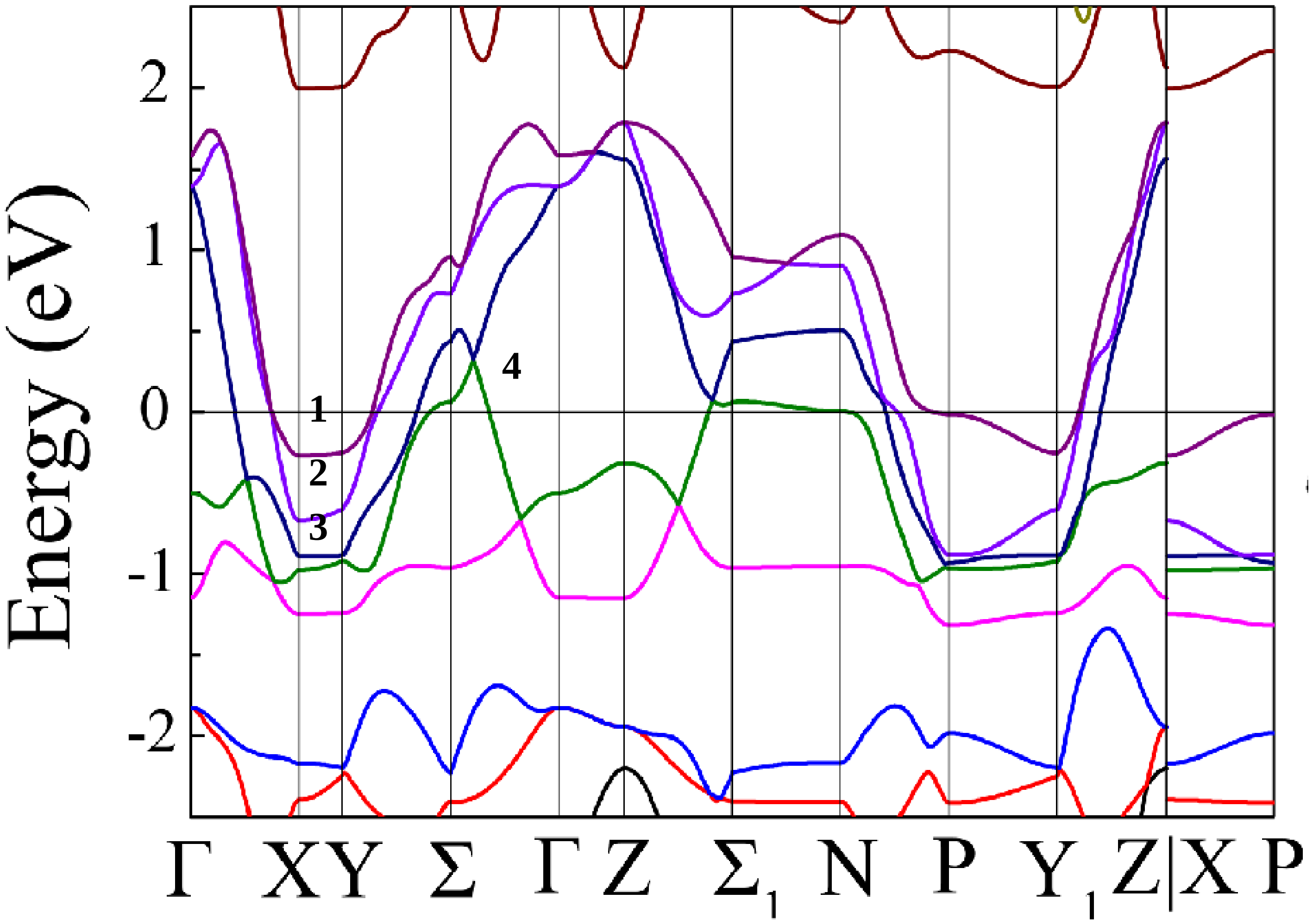
Miao Gao
Ningbo University

Xunwang Yan
Qufu Normal Univ

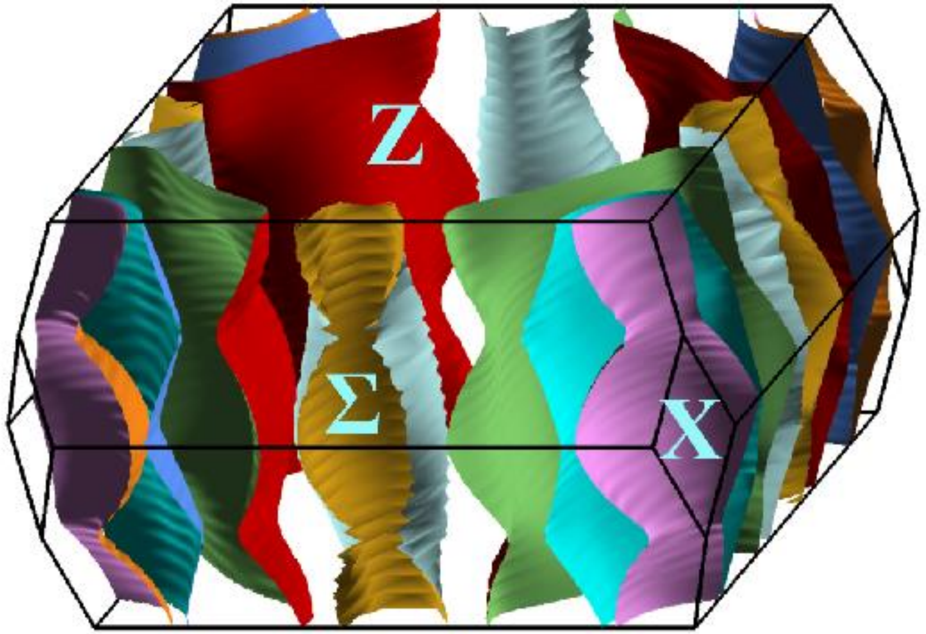
Fengjie Ma **Xinlei Zhao**
Beijing Normal University

Thank you for your attention!

$TlFeSe_2$: Band Structure in the Nonmagnetic Phase

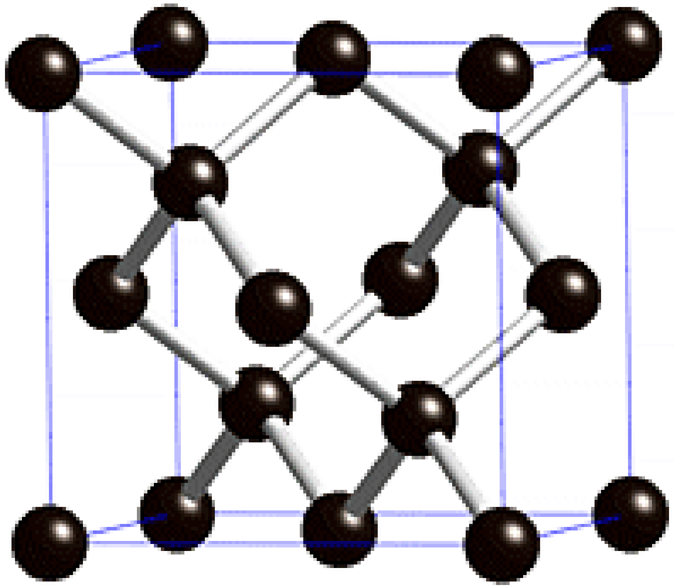


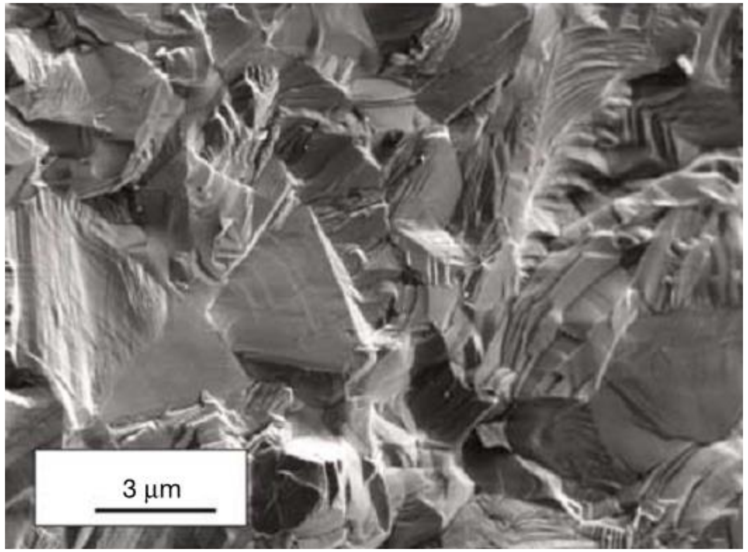
1, 2, 3 electron-type FS 4 hole-type FS



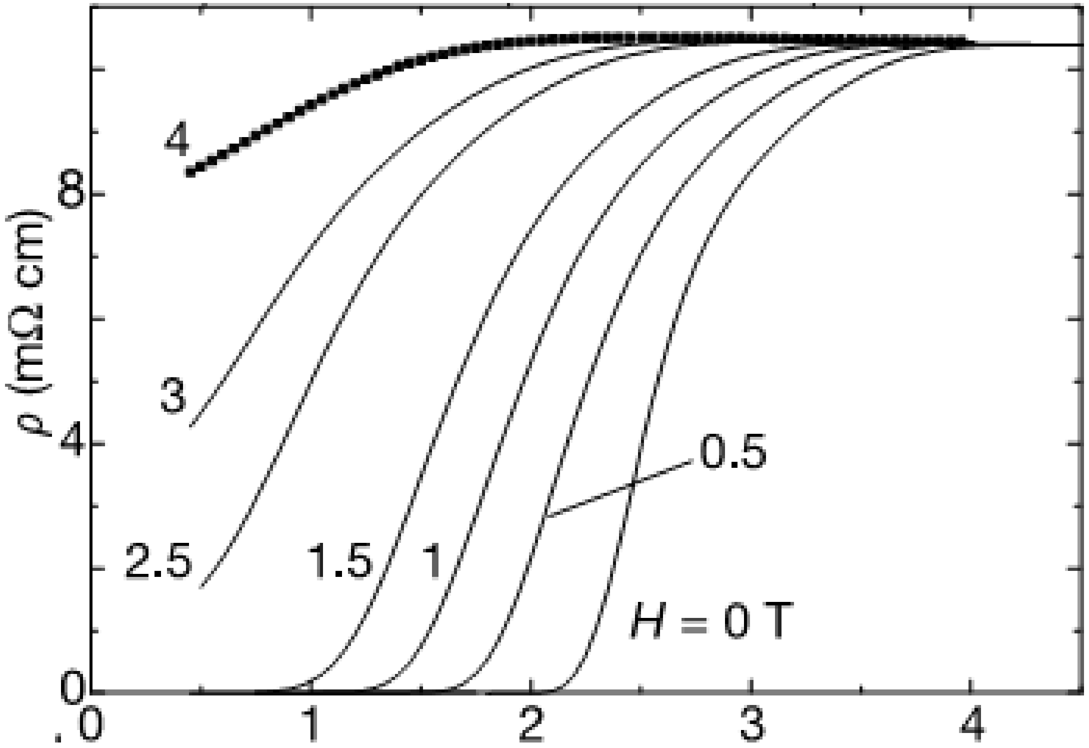
No Fermi-surface nesting

Boron doped diamond





$T_c = 4$ K   2.8% B



Low density of states at Fermi level

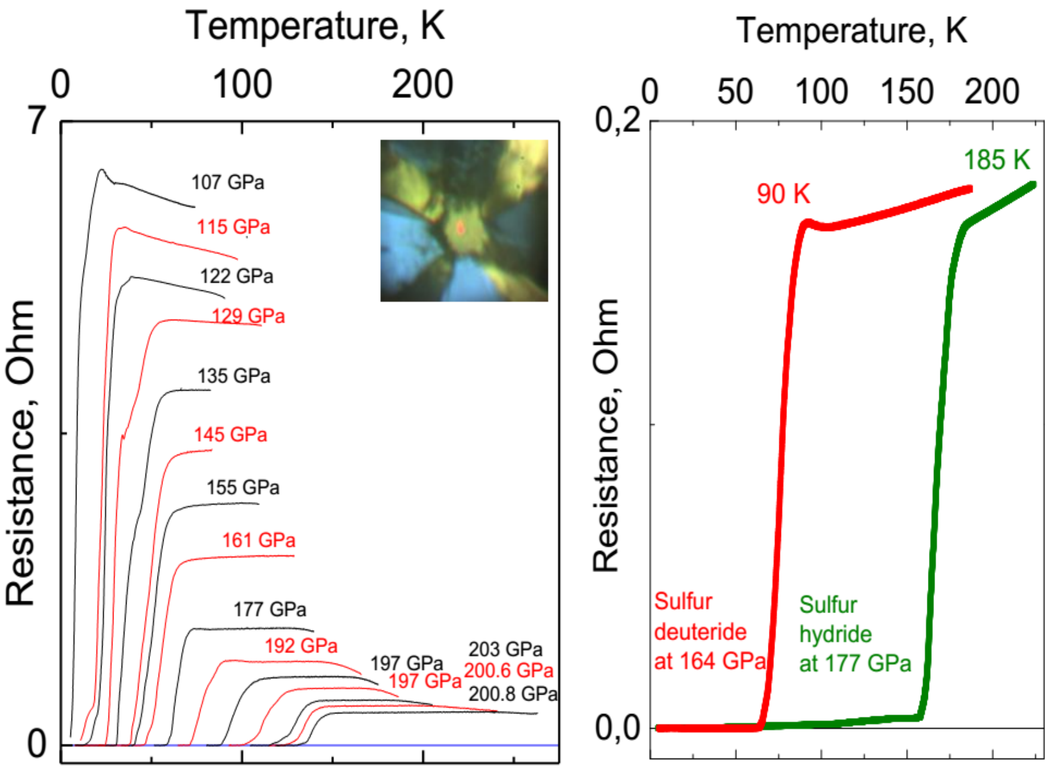
E. A. Ekimov *et al.* , Nature (London) 428, 542 (2004).

Conventional Wisdom of Raising T_c

To apply high pressure to light elements

H enriched H_3S: possible 190K superconductor at 200 GPa

1. resistivity is 50 times lower than the copper resistivity
2. T_c decreases with magnetic field
3. strong isotope shift of T_c in D_2S: Tc 185 K for H_2S, 90 K for D_2S



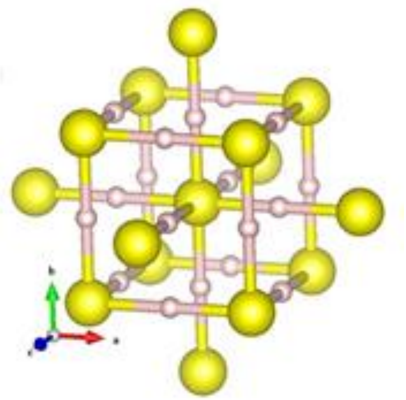
AP Drozdov, MI Eremets, IA Troyan, Nature 2015

Conventional Wisdom of Raising T_c

To apply high pressure to light elements

H enriched H_3S: possible 190K superconductor at 200 GPa

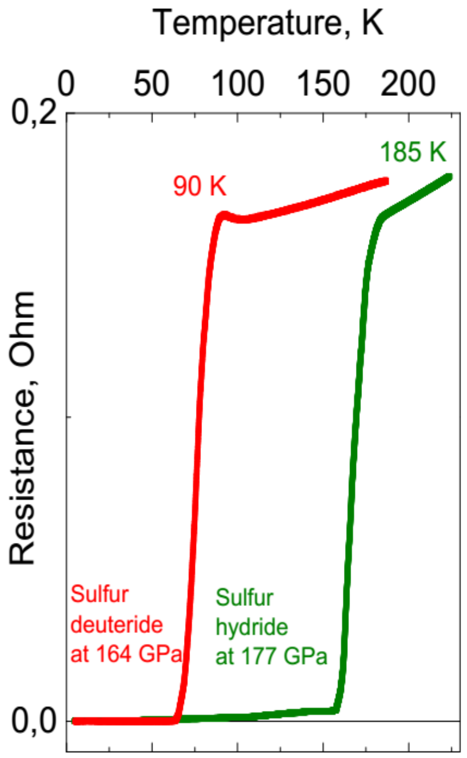
λ	ω_{log}	μ^*	T_c	*Pressure*
2.19	*1334.6* K	0.1~0.13	191-204 K	200 GPa
		0.13	184 K	250 GPa
		0.13	179 K	300 GPa



H_3S

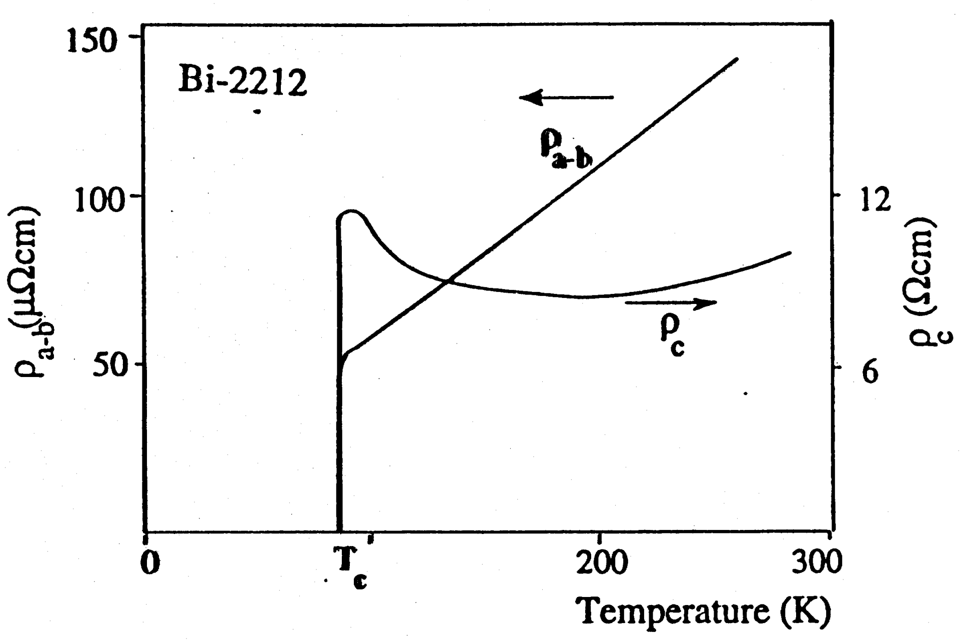
Agree with DFT prediction for H_3S

D. Duan *et al*., Sci. Reports 4, 6968 (2014)



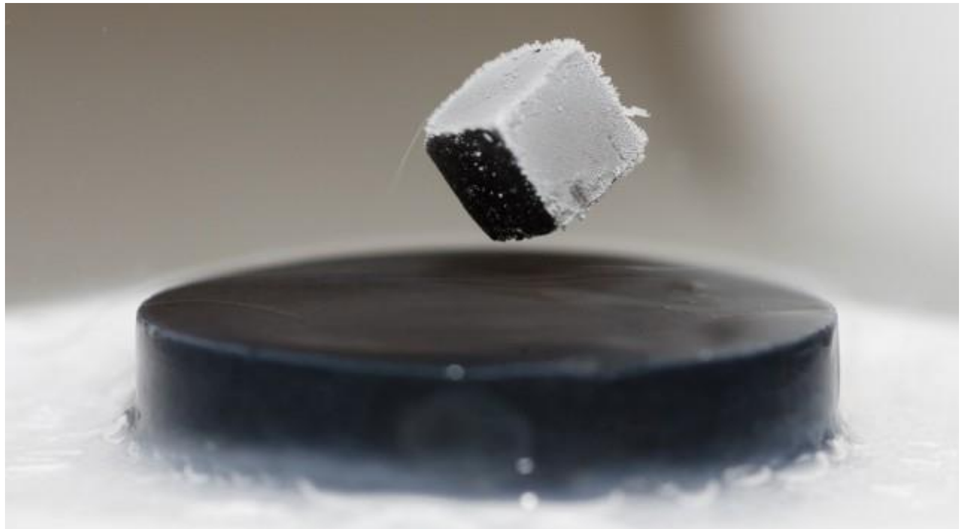
What is a superconductor?

Perfect conductor



Resistivity vanishes in the superconducting state

Perfect diamagnet



Messiner effect

Anderson-Higgs Mechanism

How to become superconducting

Electrons form Cooper pairs
via electron-phonon or other interactions

⇩

Cooper pairs condense
to form phase coherence

⇩

Superconductivity

Bardeen **Cooper** **Schrieffer**

1957