Superconductivity in B doped Silicon and diamond

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Close collaboration with :

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OUTLINE

- (short) historical revue on

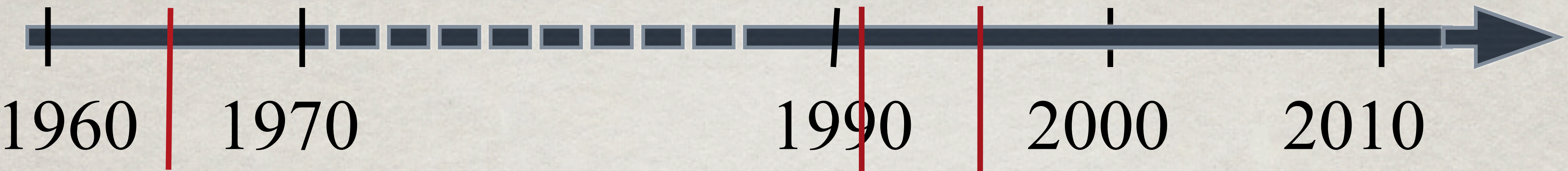
superconducting group IV superconductors

[covalent superconductors]

a new route to high temperature superconductivity....

- Diamond : superconductivity vs metal-insulator transition

- Superconducting silicon thin films



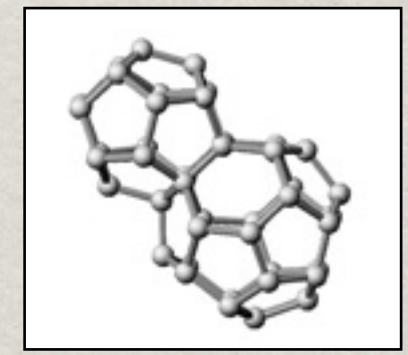
M.L.Cohen (1964)

J.F.Schooley et al. : $SrTiO_3$

R.A.Hein et al. : $Ge_{1-x}Te$

but T_c limited to a few 100mK

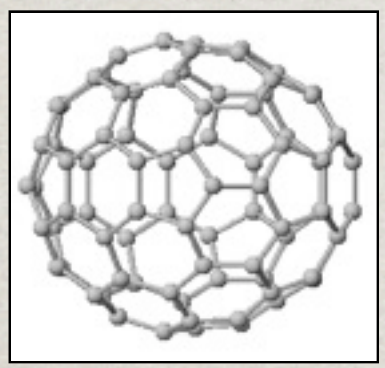
90' : Cage structures



H.Kawaji et al. (1995)

Silicon clathrates : 3D semi conductors made of face−sharing Si *n*-clusters (*n* = 20,24,28). As in standard Si, each atom is fourfold (sp3) coordinated

large doping can be obtained by intercalation in the center of the cages



R.M.Fleming et al. (1991)

C60 buckyball, mostly sp2 coordination (folded graphene), semiconducting molecular solid (face centered cubic structure)

Narrow (t_{1u}) empty band which can by filled by intercalation of alcali elements in the cavities between the balls

T_c ~ 30K in Rb_3C_{60}

T_c ~ 4K in $NaBa_2Si_{46}$

[even **7K** in Ba_8Si_{46} D.Connetable et al. 2003] electron-phonon coupling constant $\lambda_{e-ph} = N \times V_{e-ph}$

Fullerenes
N ~ 10 states/eV/spin/cell
V_{e-ph} ~ 70 meV
(λ_{e-ph} ~ 0.7)

Si-clathrates
N ~ 40 states/eV/spin/cell
V_{e-ph} ~ 20 meV
(λ_{e-ph} ~ 0.8)

V_{e-ph} can be *theoretically* increased by

reducing the size of the ball
(i.e. increasing the **sp3 character**)

V_{e-ph} ~ 210 meV in C_{28}
(N.Breda et al. 2000)

replacing Si by **C**

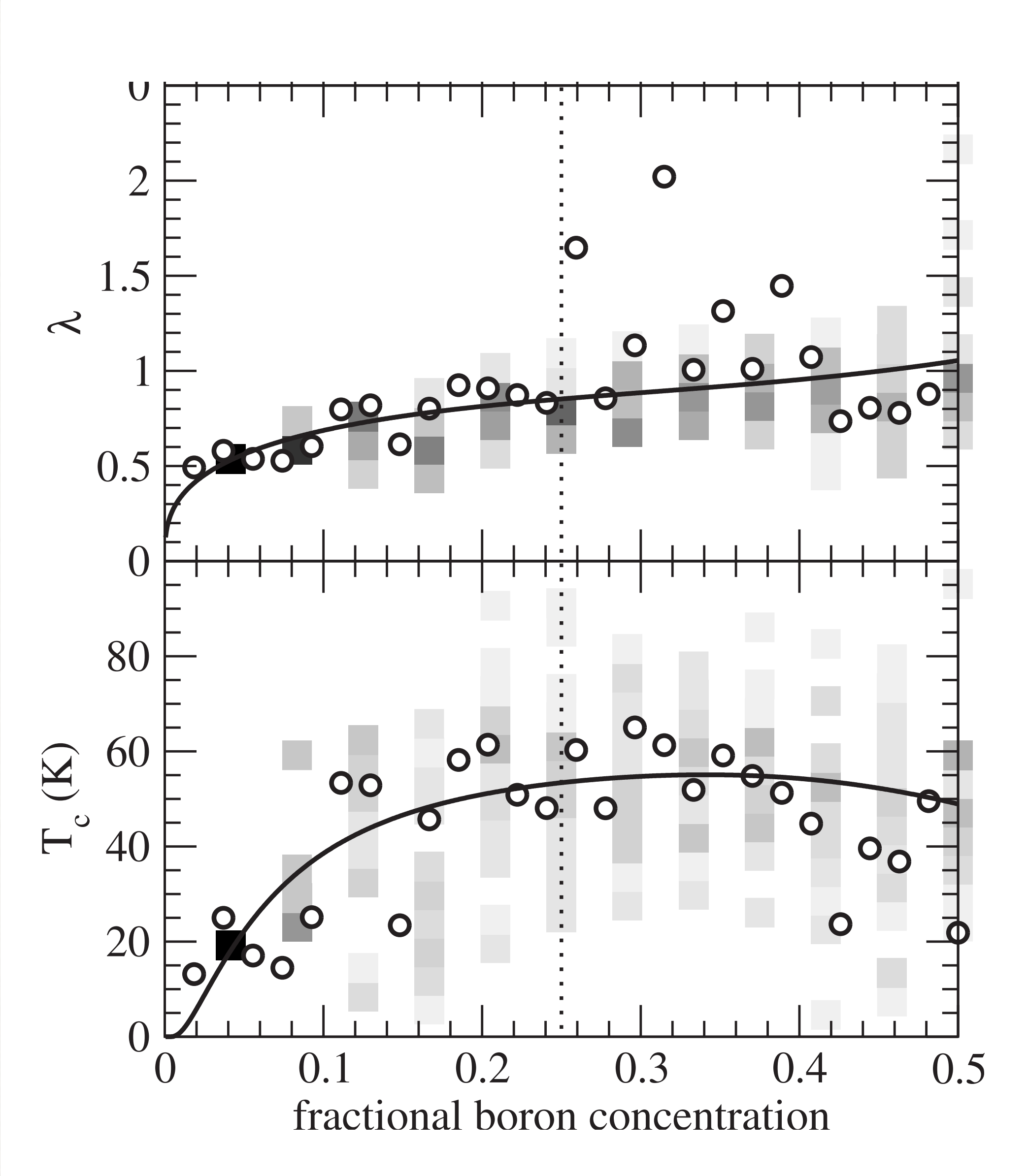
V_{e-ph} ~150-250 meV
(D.Connetable et al. 2003)

expected T_c above 200K !!!

B doped **Diamond** : BC_{53} (X.Blase et al. 2003)

V_{e-ph} ~ 280 meV ...

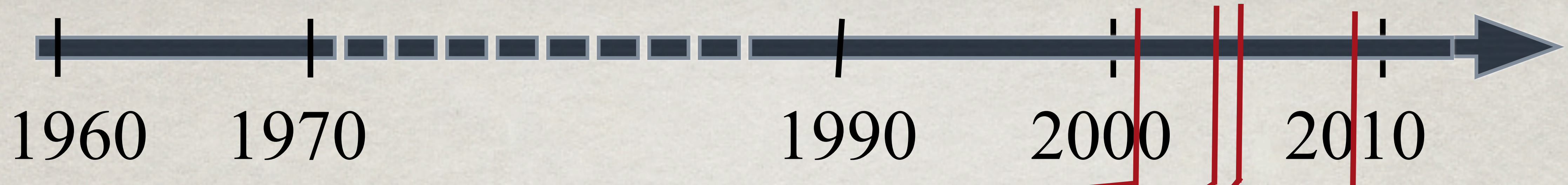
... and N depending on the Boron concentration



Moussa et al. 2008
(see also Calandra et al. 2008)

T_c *could* reach ~60K around ~30at-%

Note : interesting $Li_{1-x}BC$ system : semiconducting for x=0, *should* become superconducting for x>0.2 with **T_c ~ 150K** for x ~ 0.5 (Rosner et al. 2002)



MgB_2 Nagamatsu et al. 2001

B-hexagonale structure (silimar to graphite)
but σ (sp2) band shifted to E_F
due to presence of Mg^{2+}

$T_c \sim 39K$

CaC_6, YbC_6

Weller et al. 2005

Intercalated graphite
intercalant (~ free electron) ζ-band

$T_c \sim 11K$

B doped diamond

Ekimov et al. 2004

superconductivity (in sp3 band)
appears at the onset of
Metal Insulator Transition

T_c up to 10K ($n_B < 5\%$*)

Si:B

Bustarret et al. 2007

$T_c < 1K$

* for large doping :
- clustering of borons into inactive dimers
- increase of the interstitial boron content

and also B:SiC (Renet al.2007) or Ga:Ge (Herrmannsdorfer et al. 2009)

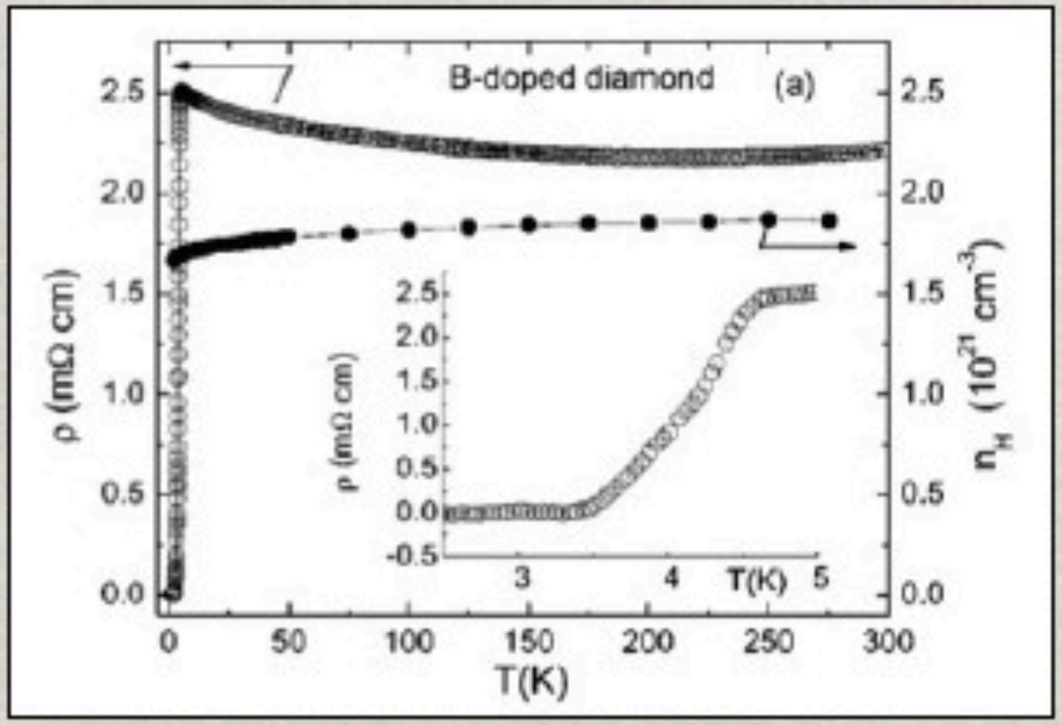
Superhardness : the B:C:N triangle
C (80-130 GPa)
B_4C (30 GPa), BN (62 GPa), BC_2N (76 GPa)

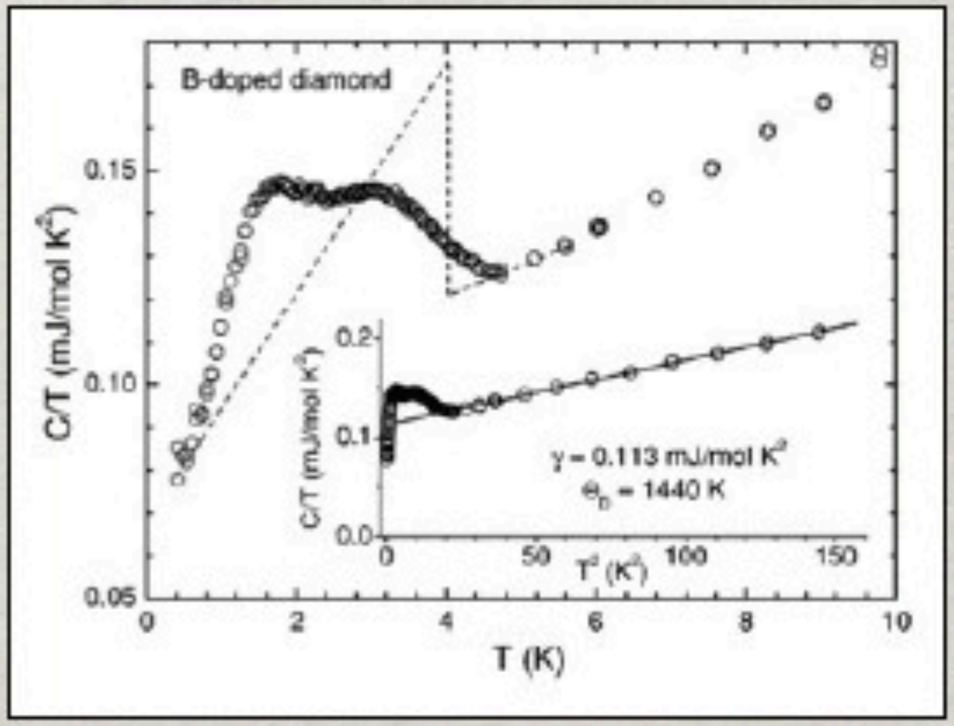
HPHT : 2500-2800 K, 8-9 GPa, 5 s
Graphite + B_4C $\longrightarrow$ B-doped diamond + B_4C traces (Ekimov et al. 2004)

Doping level : 2-3 at % i.e. 3-5 10^{21} B/cm^3

T_c ~3K

Specific heat measurements confirmed bulk superconductivity (not filamentary) [Sidorov et al. 2005]





rapidly confirmed in [thick] epitaxial films (grown by plasma assisted CVD)

001-oriented type Ib **diamond substrates**

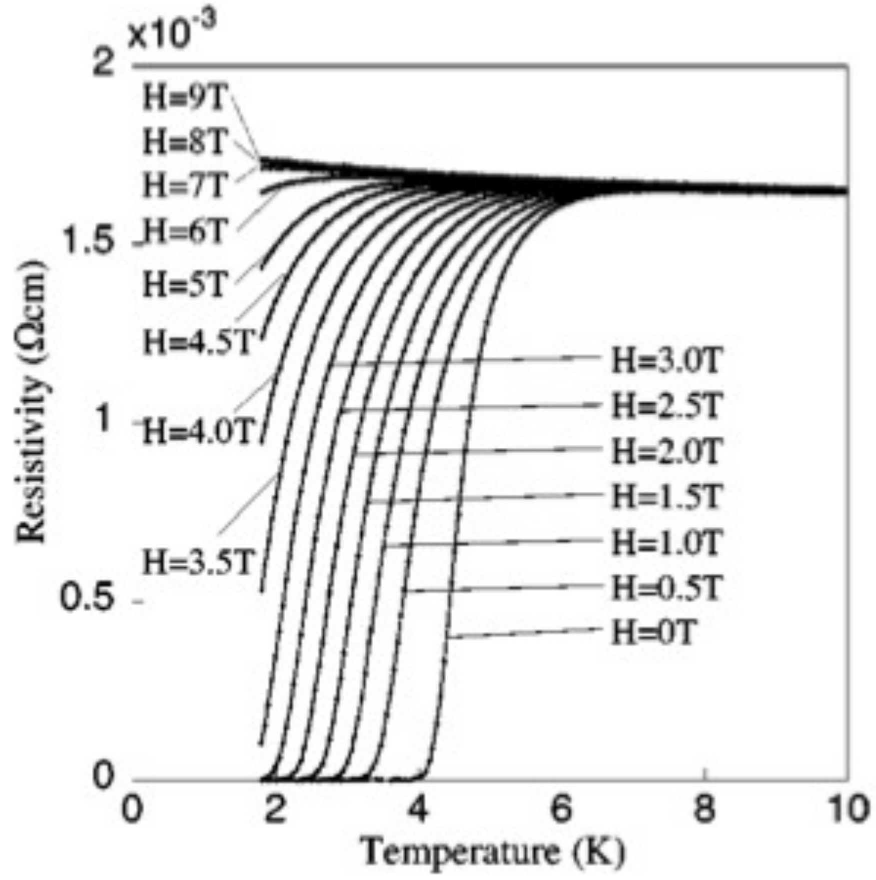
Hydrogen plasma + Methane (4%)
-> 0.5 µm-thick **buffer layer** of nonintentionally doped material

Diborane introduced in vertical silica wall reactor with [B]/[C] from 1500 to 3000 ppm

High quality **µm-thick p-type diamond** epilayers

x-ray diffraction : (shifted) narrow lines
FWHM ~ 10 arc sec ([004] peak) ~ substrate

but n_B (still) < 2.5 at-%

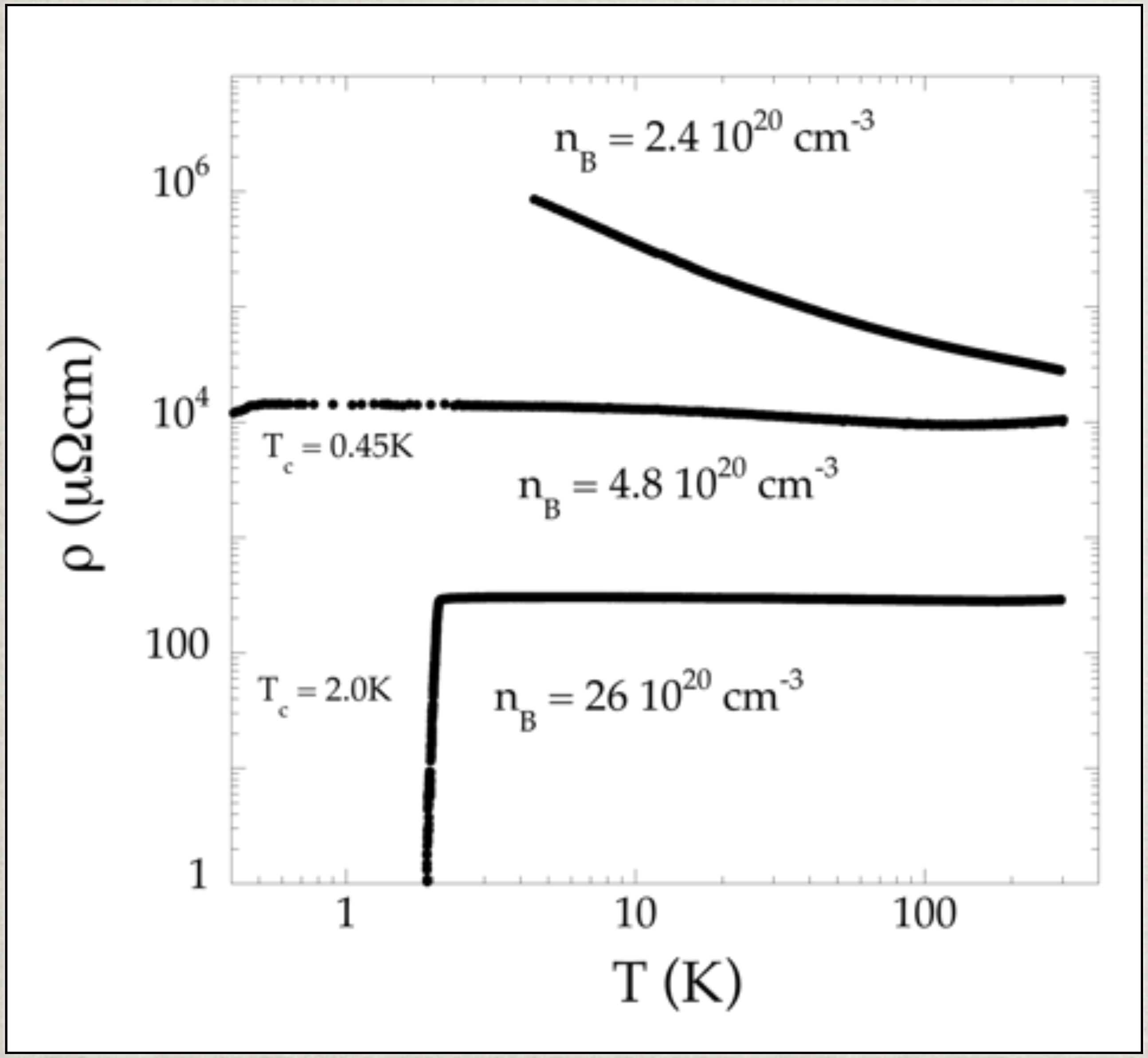


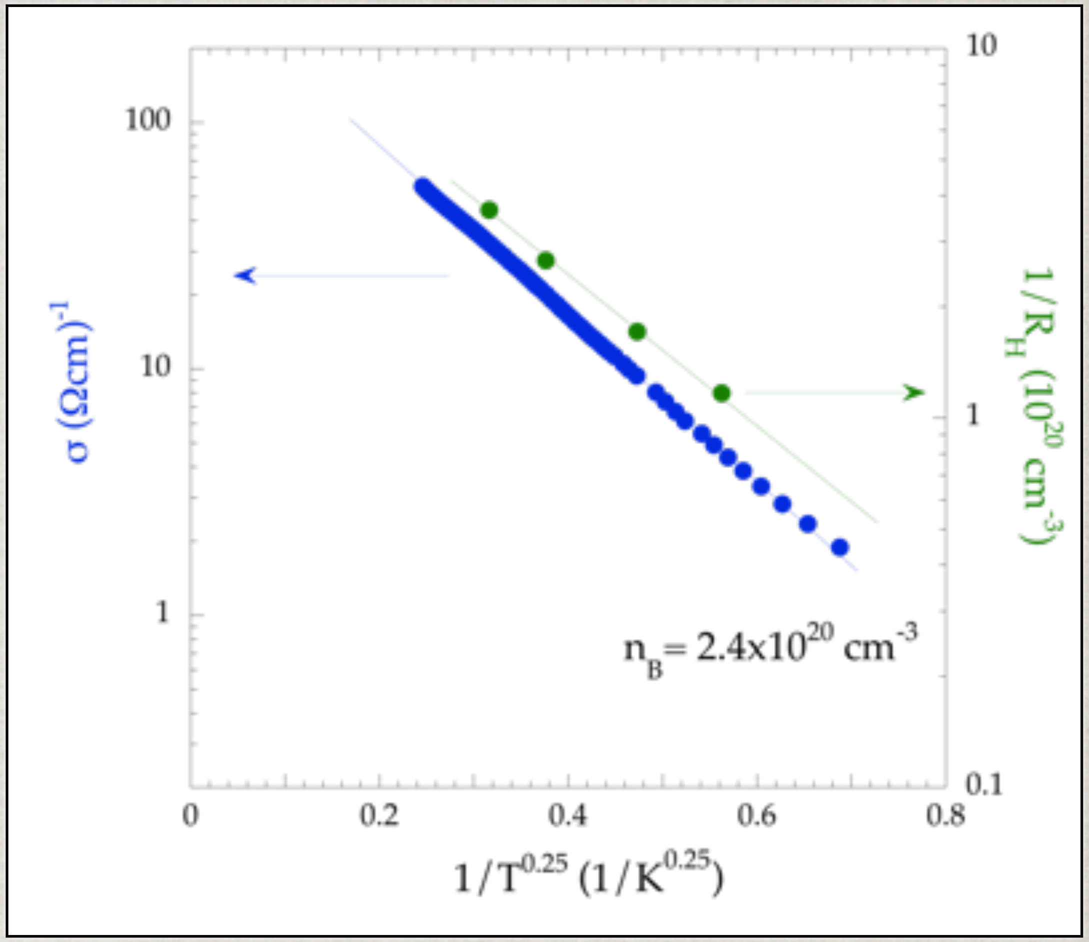
Y.Takano (2004)

[111] oriented

$H_{c2}(0)$ ~ 10T

T_c up to ~10K for $10^{22}cm^{-3}$ = 5 at-%





$$\sigma = \sigma_0 exp[-(T_0/T)^{1/4}]$$

$$R_H = R_{H,0} exp[-(T_{0,H}/T)^{1/4}]$$

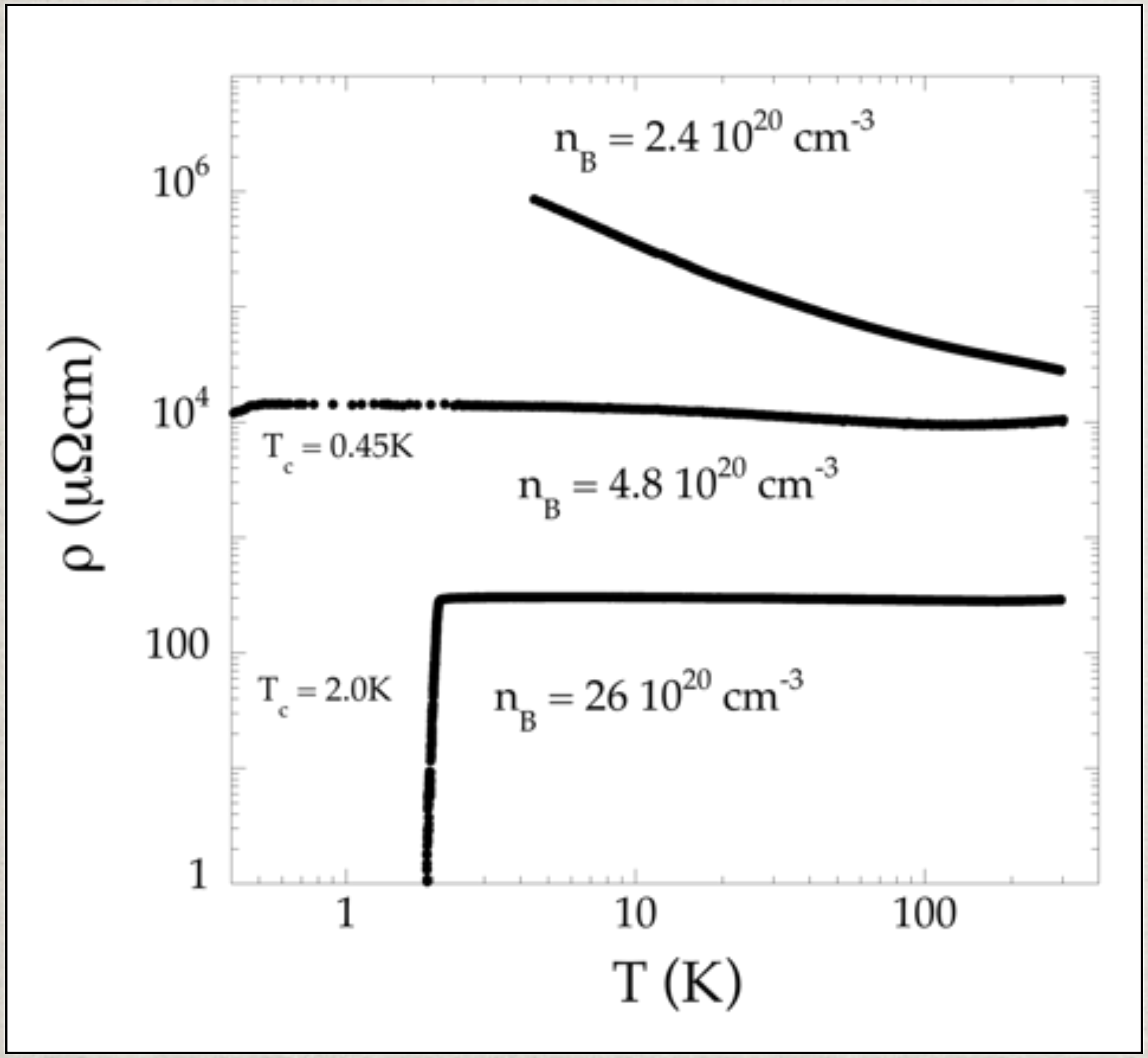
with $[T_{0,H}/T_0]_{th} = 0.15$

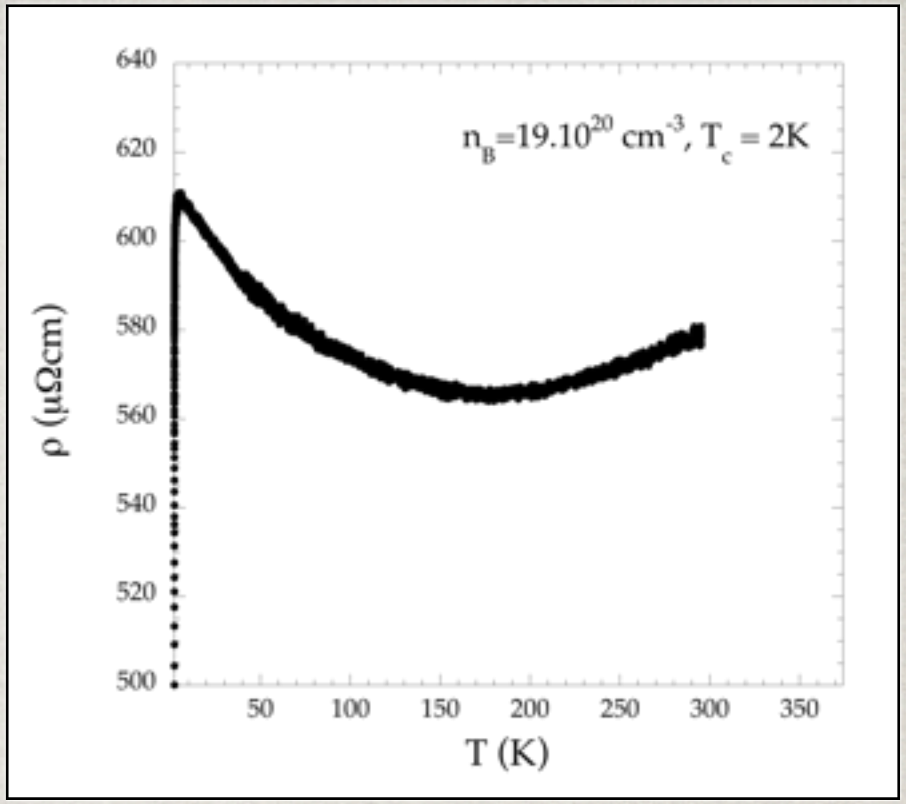
$n < n_c \sim 4.5 10^{21}$ cm^{-3}

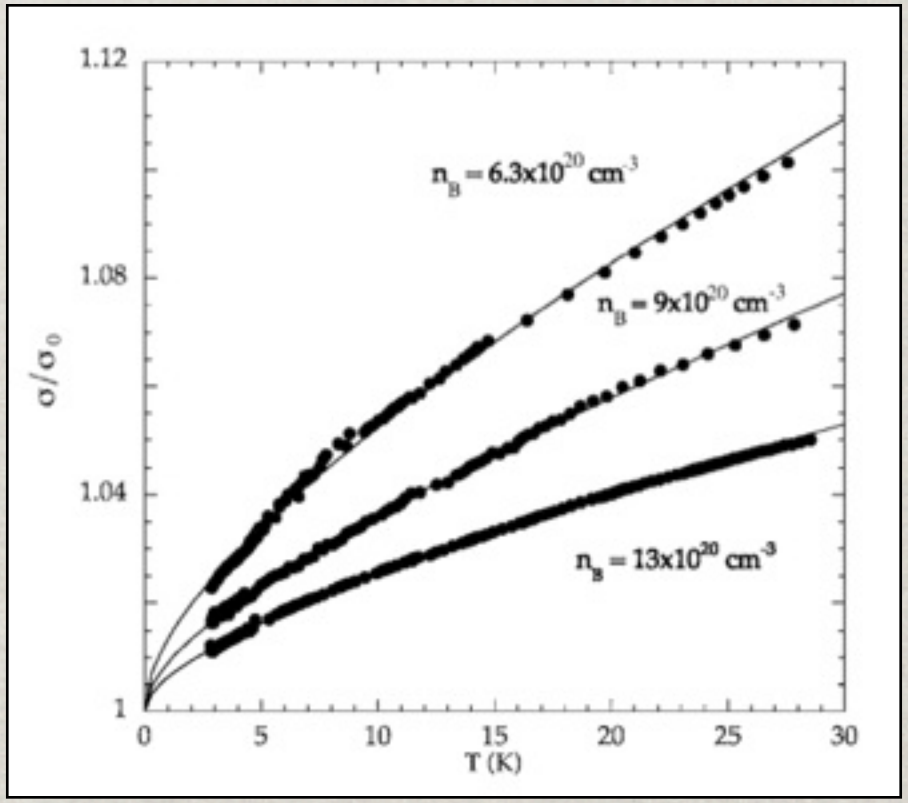
Variable Range Hopping conductivity

and $[T_{0,H}/T_0]_{exp} = 500/3700 \sim 0.13$
($n_B = 2.4.10^{21}$ cm^{-3})

Quantum Interference effects
(weak localisation +e-e interactions)



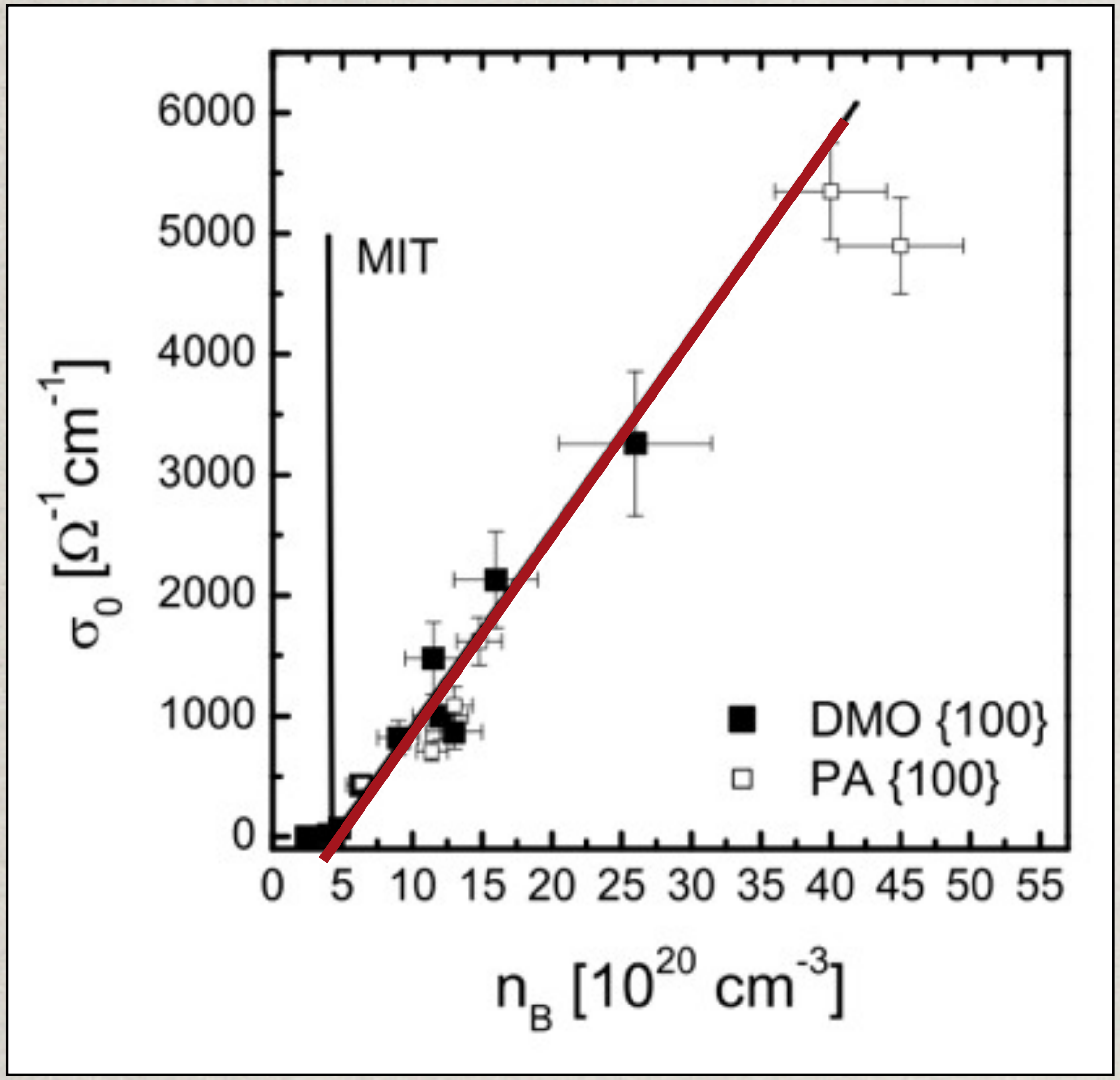


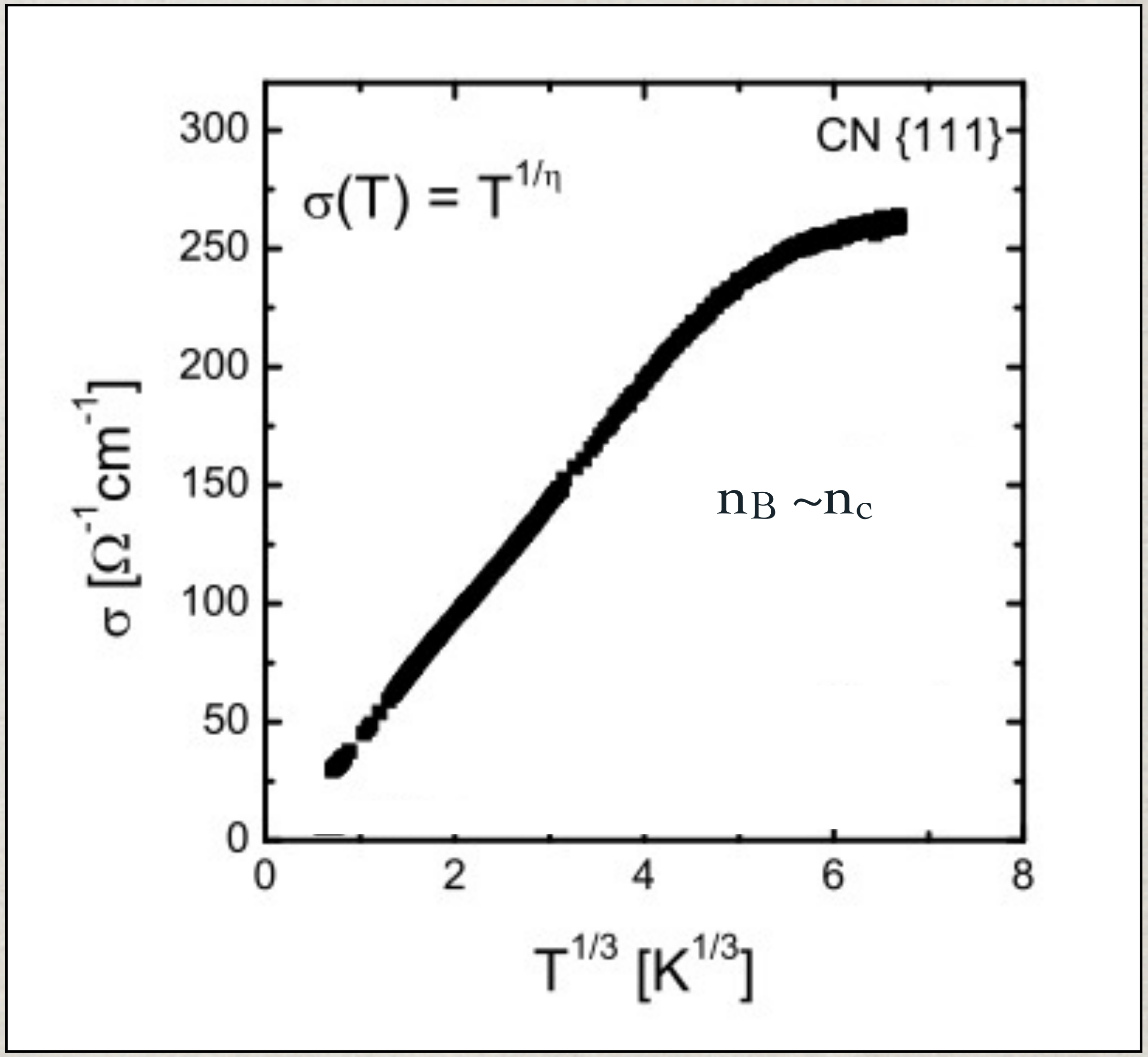


$n > n_c \sim 4.5 10^{21}\ cm^{-3}$ (~ 0.25 at-%)

metal with E_F lying in the valence band of the diamond
(Yokoya et al. 2005)

$$\sigma = \sigma_0 + AT^{1/2} + BT$$





$$\sigma_0 = 0.1(e^2/\hbar)(1/\xi)$$

$$a^*/\xi = (n_B/n_c - 1)^\nu$$

where a* is the Bohr radius ~ 3.5A

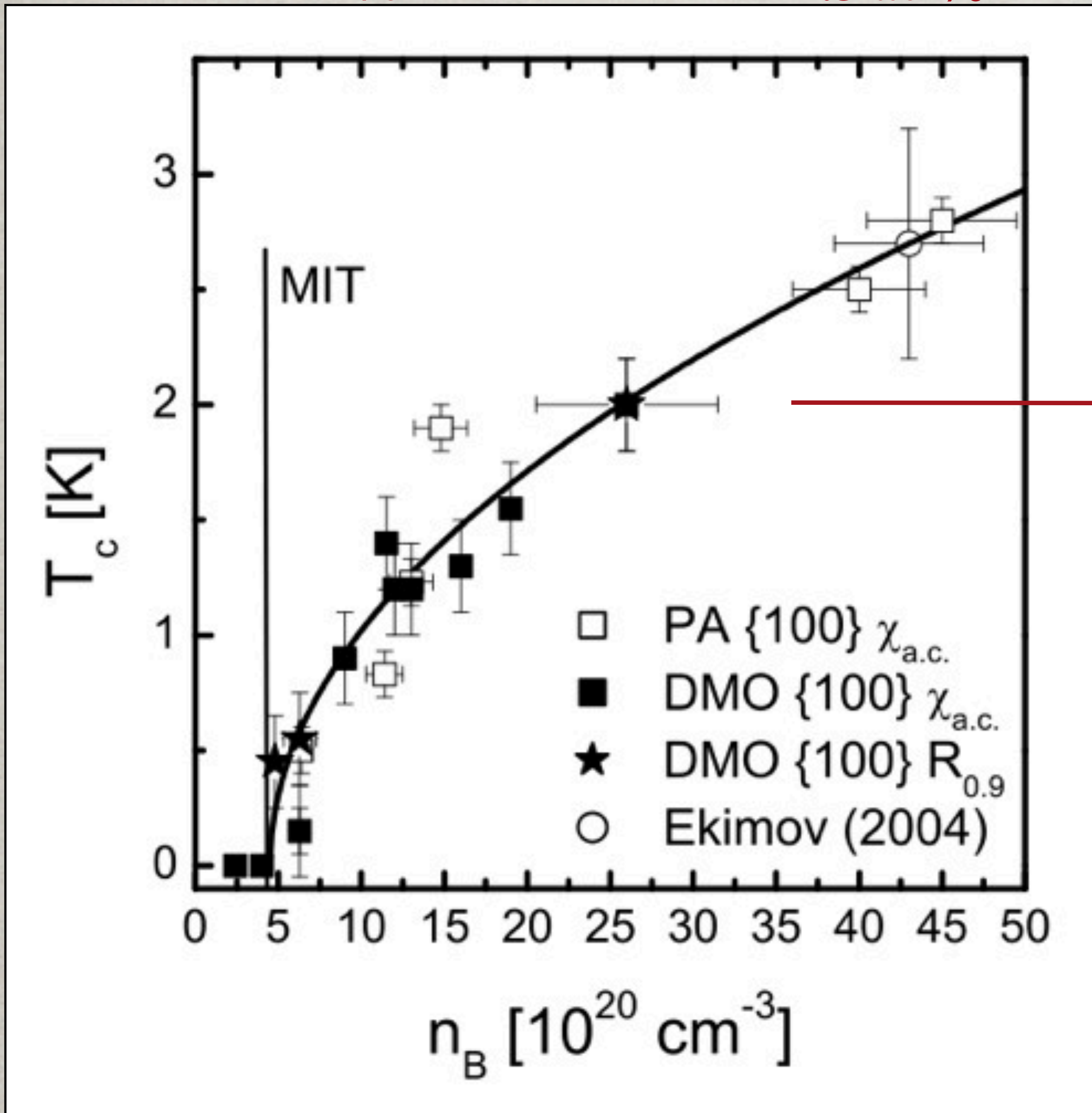
$$\nu = 1$$

$$E \propto 1/\xi^\eta$$

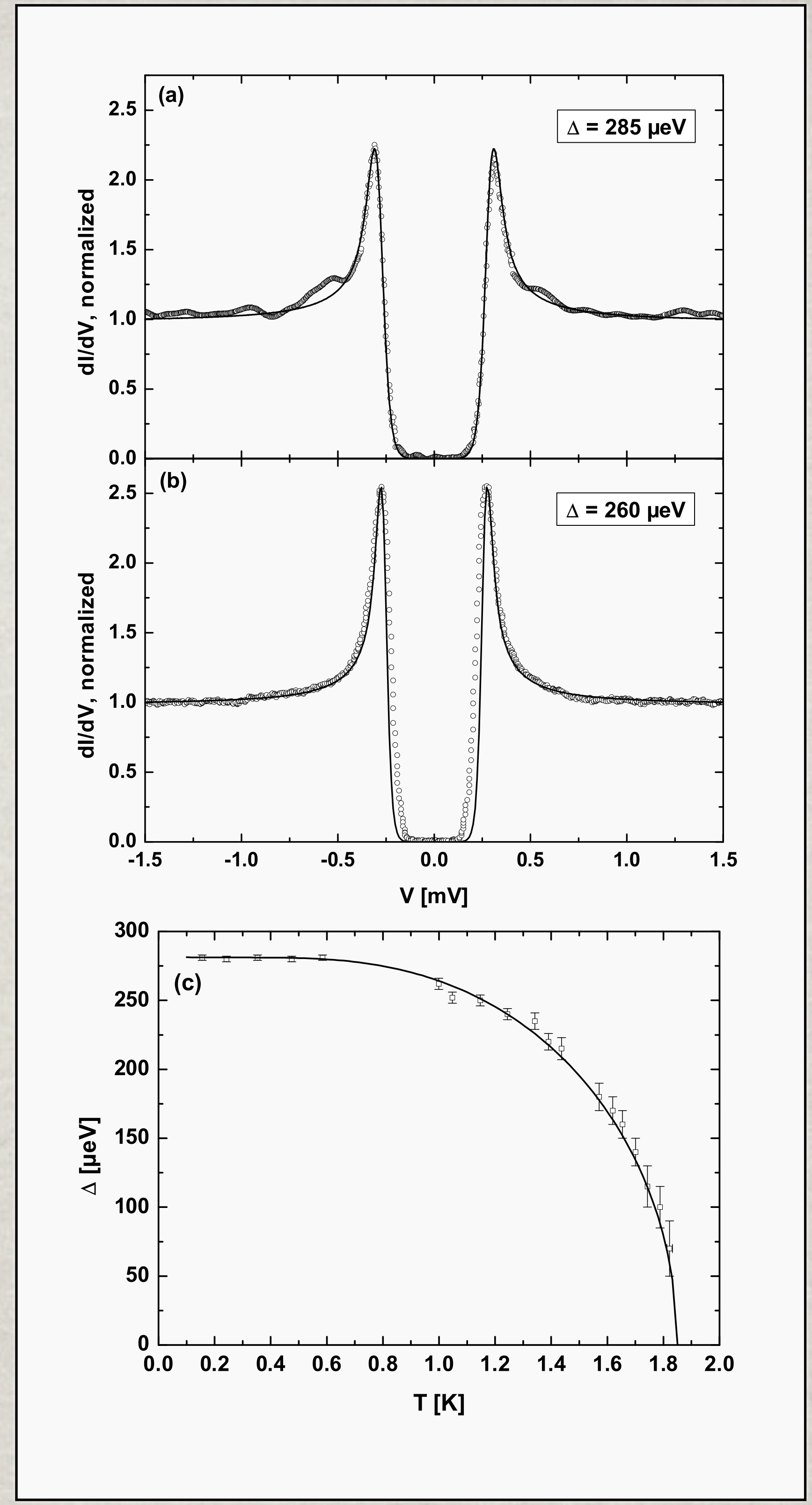
for $n_B = n_c$

$$\sigma \propto T^{1/\eta}$$

$$\eta \sim 3$$



T.Klein et al. (2007) - P.Achatz (2008)



B.Sacépé et al. (2006)

T_c remains *surprizingly high* close to n_c

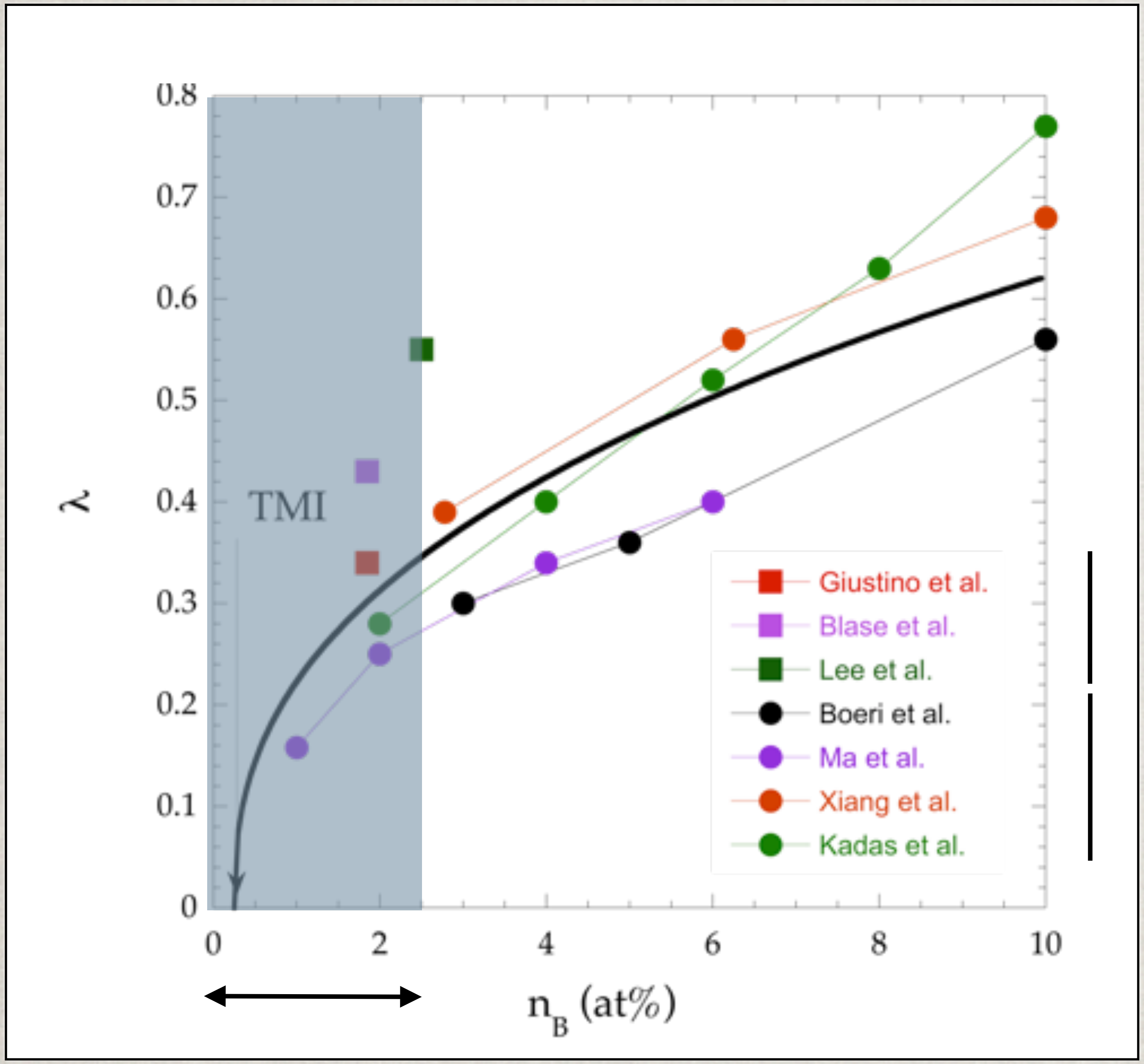
$$T_c \propto (n_B/n_c - 1)^{\beta}$$

$$\beta \sim 0.5 - 0.6$$

Fully open gap with

$\Delta/kT_c \sim 1.7$ i.e. close to BCS value

ab initio calculations -> λ



supercell method

virtual cristal approximation

experimental range
for T_c measurements
poor overlap between
doping ranges

$$T_c = \omega exp[-\frac{1+\lambda}{\lambda - \mu^*(1+\lambda)}]$$

but *unknown* μ* coefficient
(retarded Coulomb pseudopotential)

$$\mu^* = \frac{\mu}{1 + \mu ln(\omega_{el}/\omega_{ph})}$$

standard metals

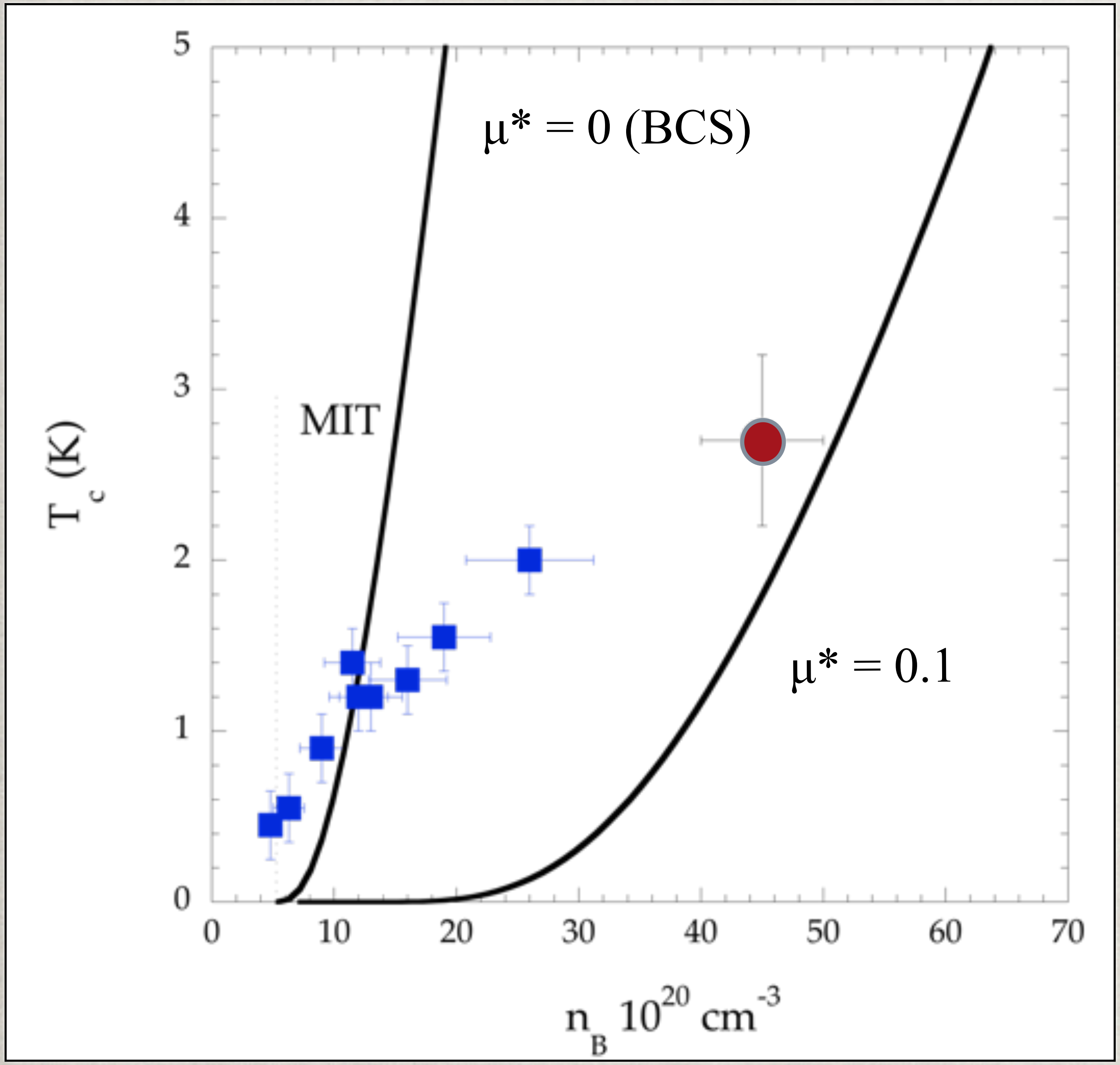
$\omega_{el}/\omega_{ph} \sim E_F/k_B\theta_D \sim 100$ leading to μ* ~ 0.15 (< μ)

diamond

$\omega_{el}/\omega_{ph} \sim E_F/k_B\theta_D < 3$

inefficient retardation effects μ* ~ μ
(similar effect in fullerenes for which μ*~ 0.3 remains close to μ ~ 0.4)

and μ is expected to tends towards 0 at the MIT ?



very reasonable agreement
between calculations and
T_c obtained by Ekimov et al. (2004)
still taking $\mu^* \sim 0.1$

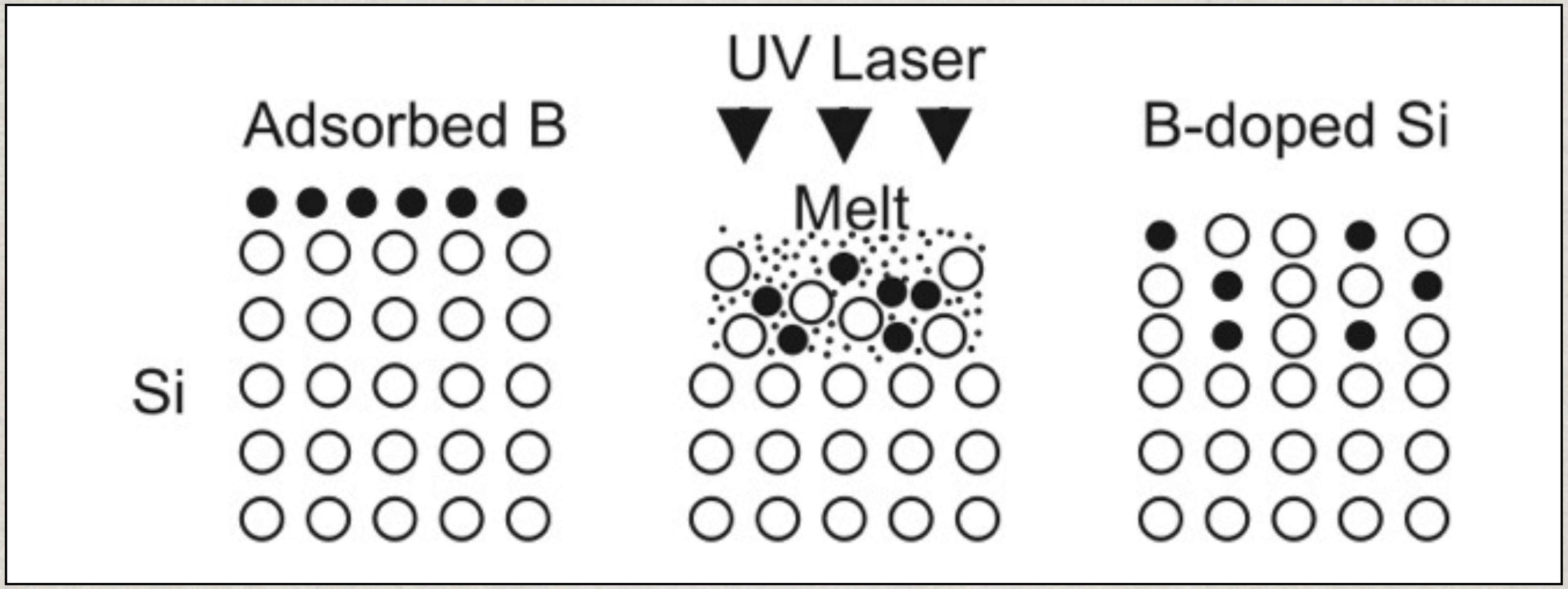
but for lower n_B values T_c much larger
than calculated values

can be associated with reduced μ (i.e. μ*)
values in the vicinity of MIT

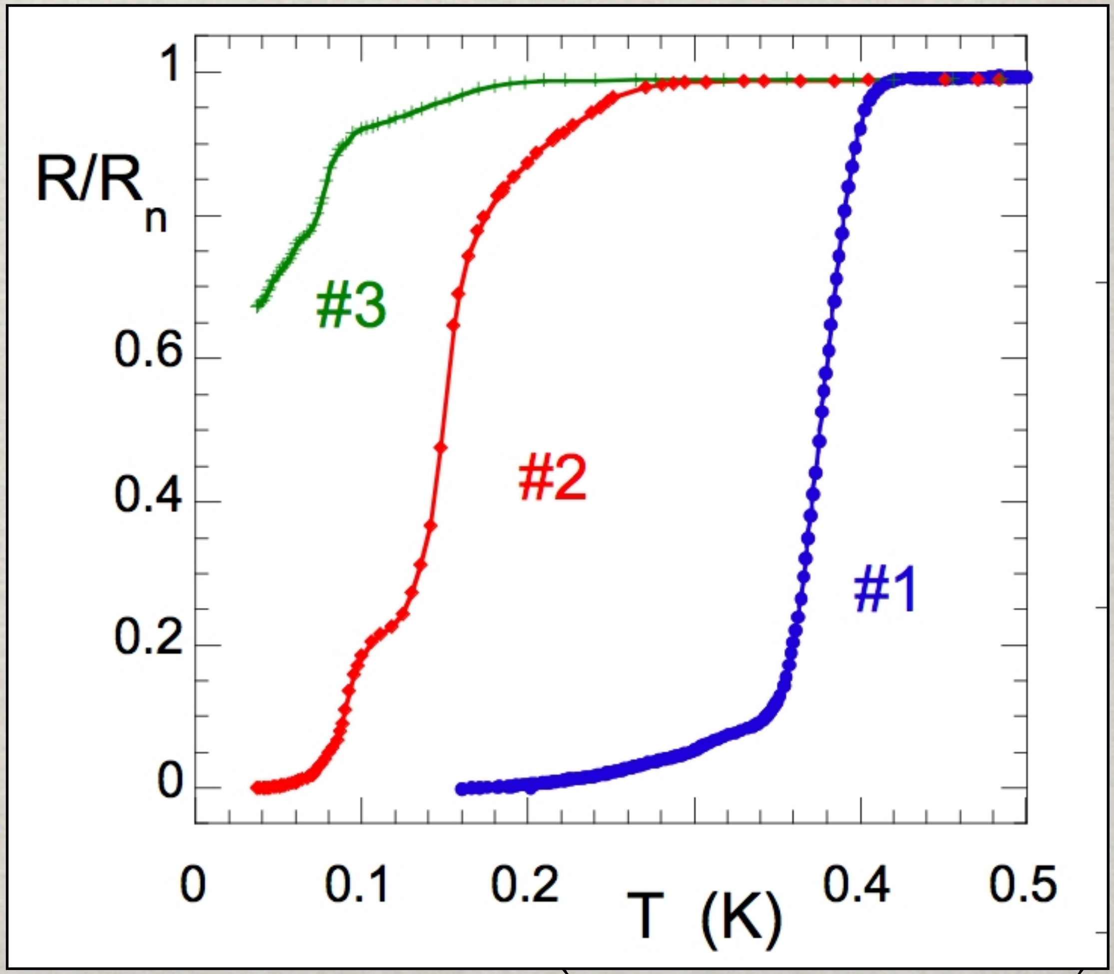
what about SILICON
$n_c \sim 10^{18}$ cm^{-3}
but **no superconductivity**
observed up to
$n_B \sim 5 10^{20}$ cm^{-3}
= SOLUBILITY LIMIT

-> Gas Immersion Laser Doping [IEF, Paris]

OUT OF EQUILUBRIUM TECHNIQUE



Recristalization rate ~ 10^{10} K/s



n_B increases with number of laser pulses

thickness of doped top layer increases with pulse duration (and laser energy)
50ns (900mJ/cm^2) <=> **100nm)**

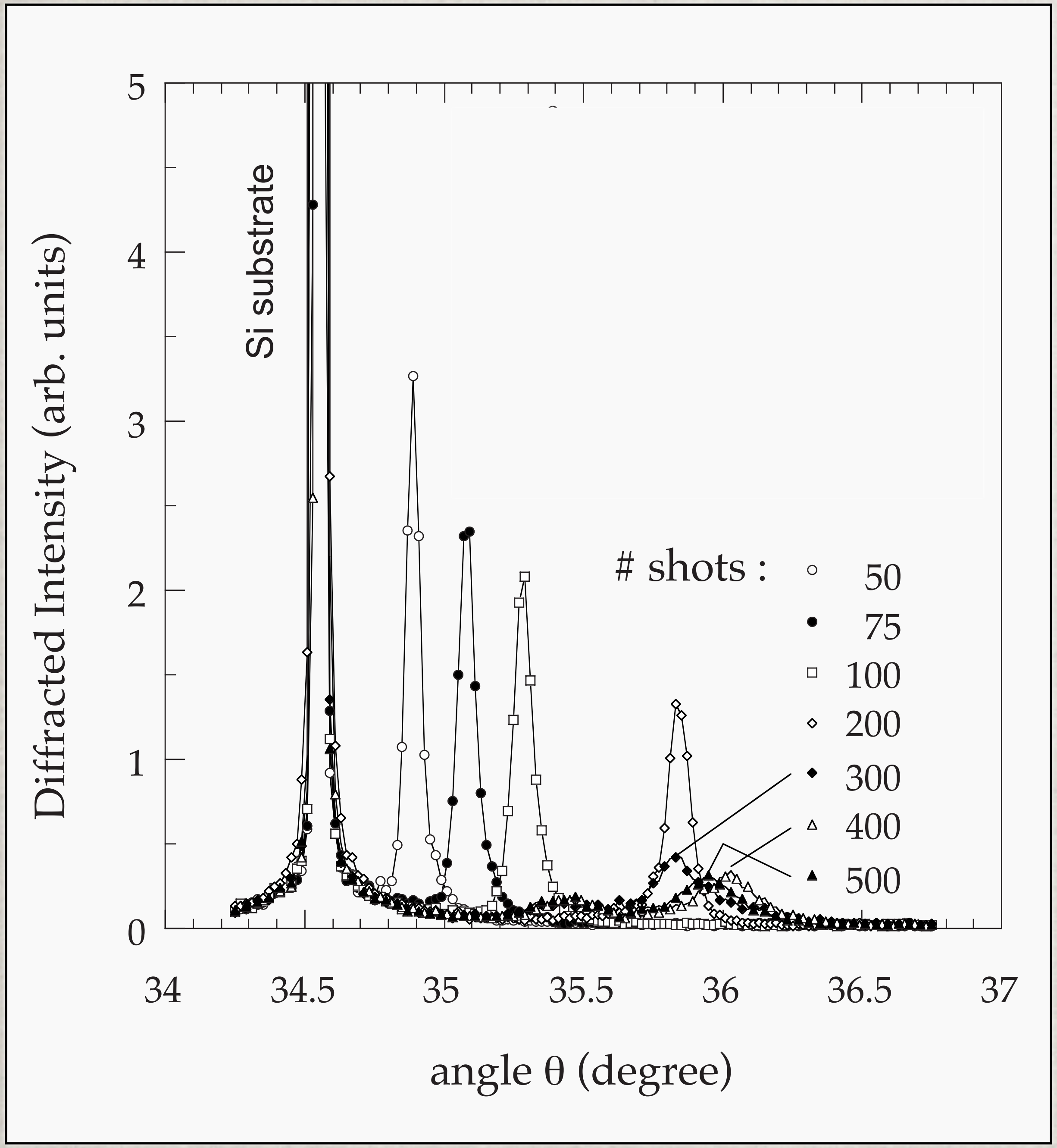
170 nm-thick 4-5 at%

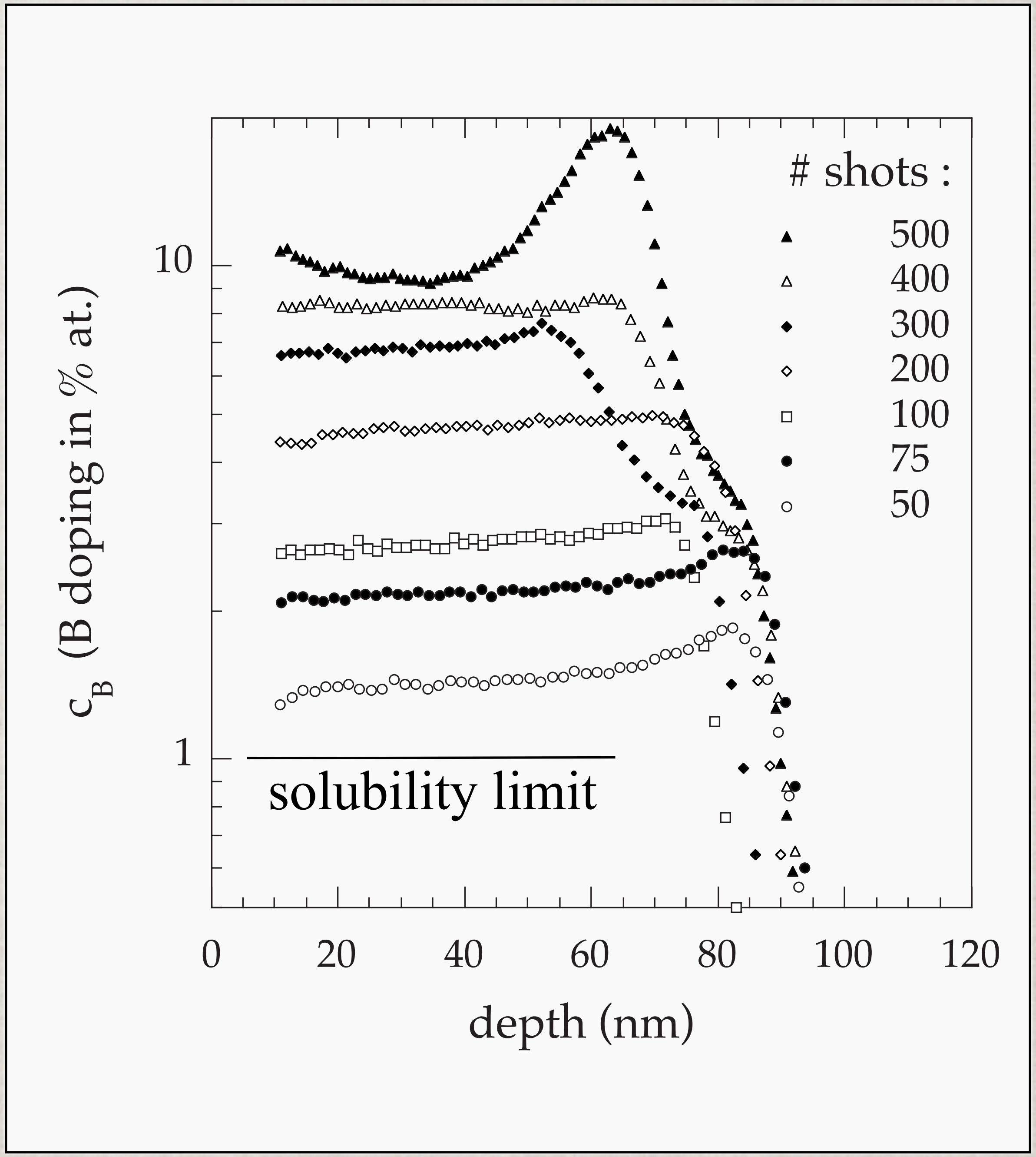
30 nm-thick 7.5 at%

35 nm-thick 5 – 9 at%

E.Bustarret
C.Marcenat et al. (2004)

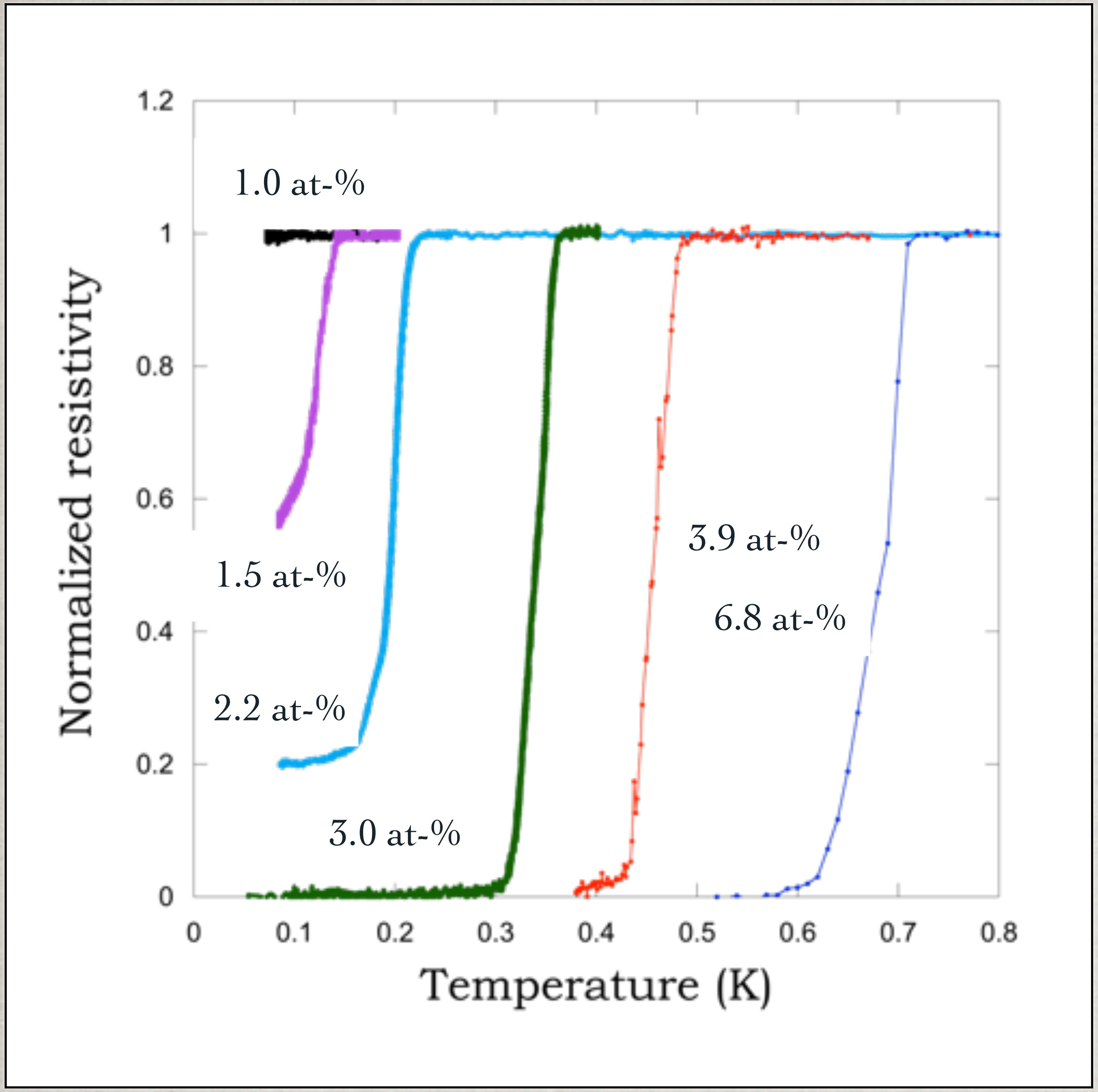
systematic study of $T_c(n_B)$ in a serie of 80nm thin films





X-rays : well defined (shifted) [004] peaks up to 200 shots

SIMS : homogenenous doping level up to 200 shots = 4.5 at% ~ 2.2 $10^{21}cm^{-3}$

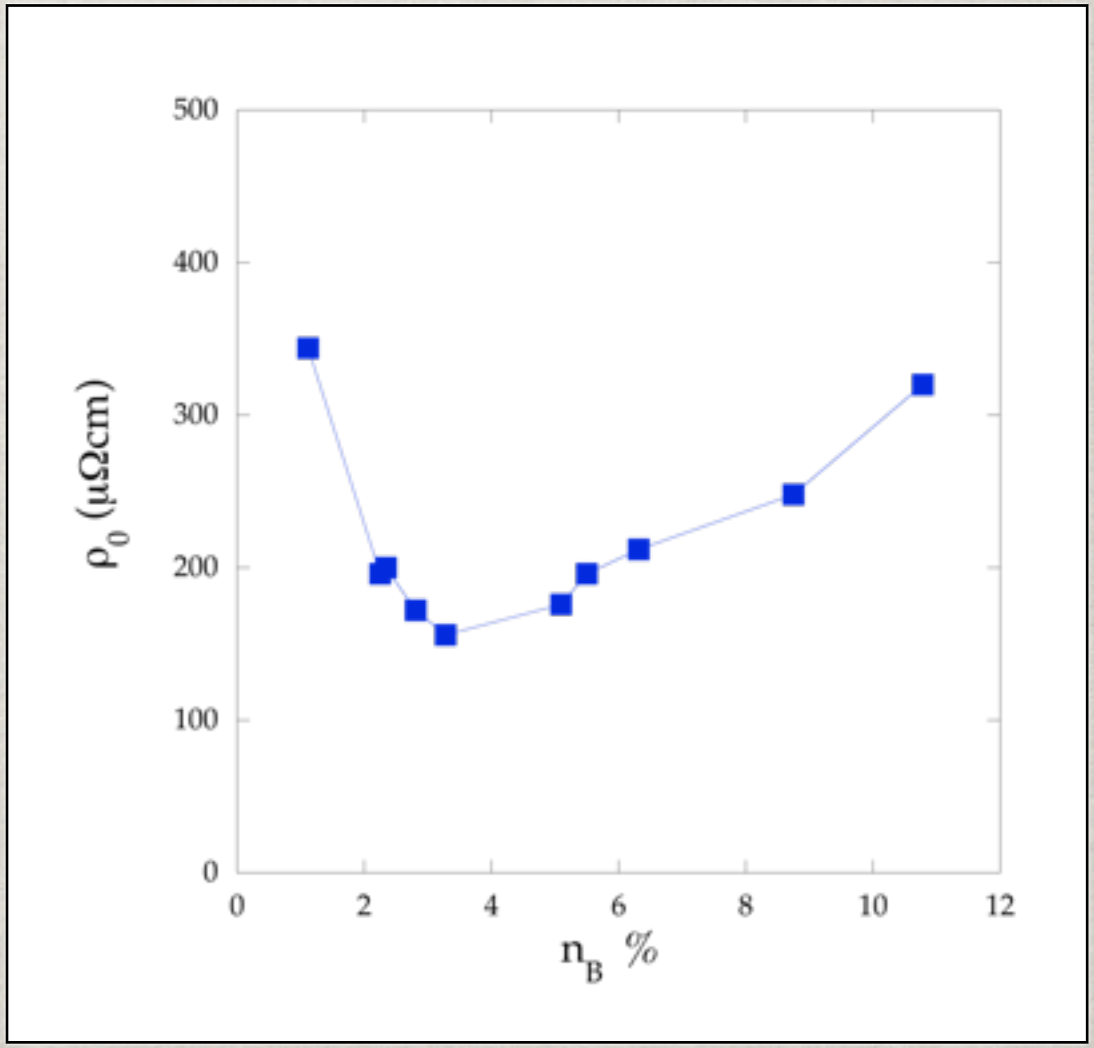


BAD METAL

$\rho_0 \sim 200\ \mu\Omega cm$

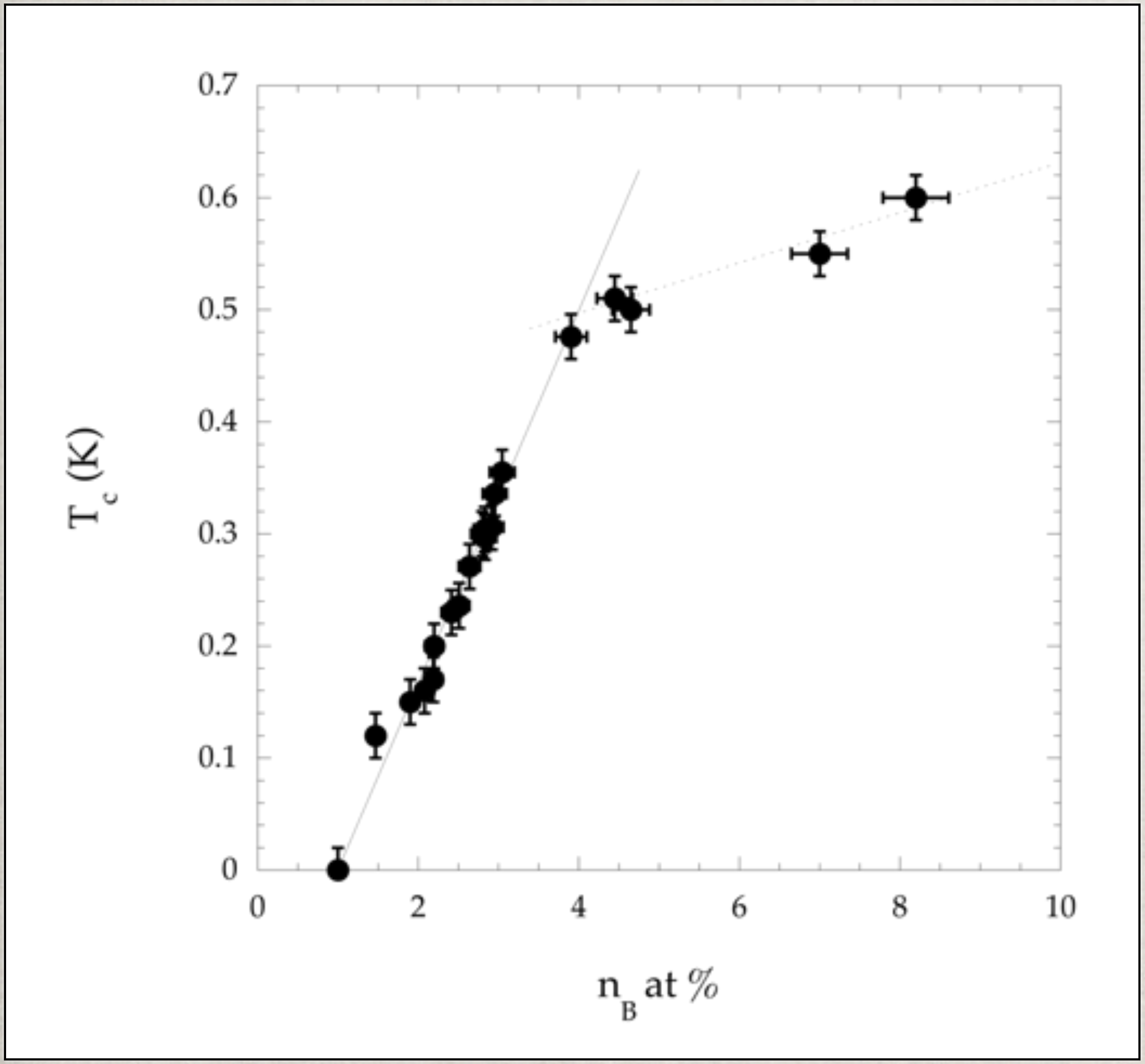
R(300K)/R(4K) ~ 1.2

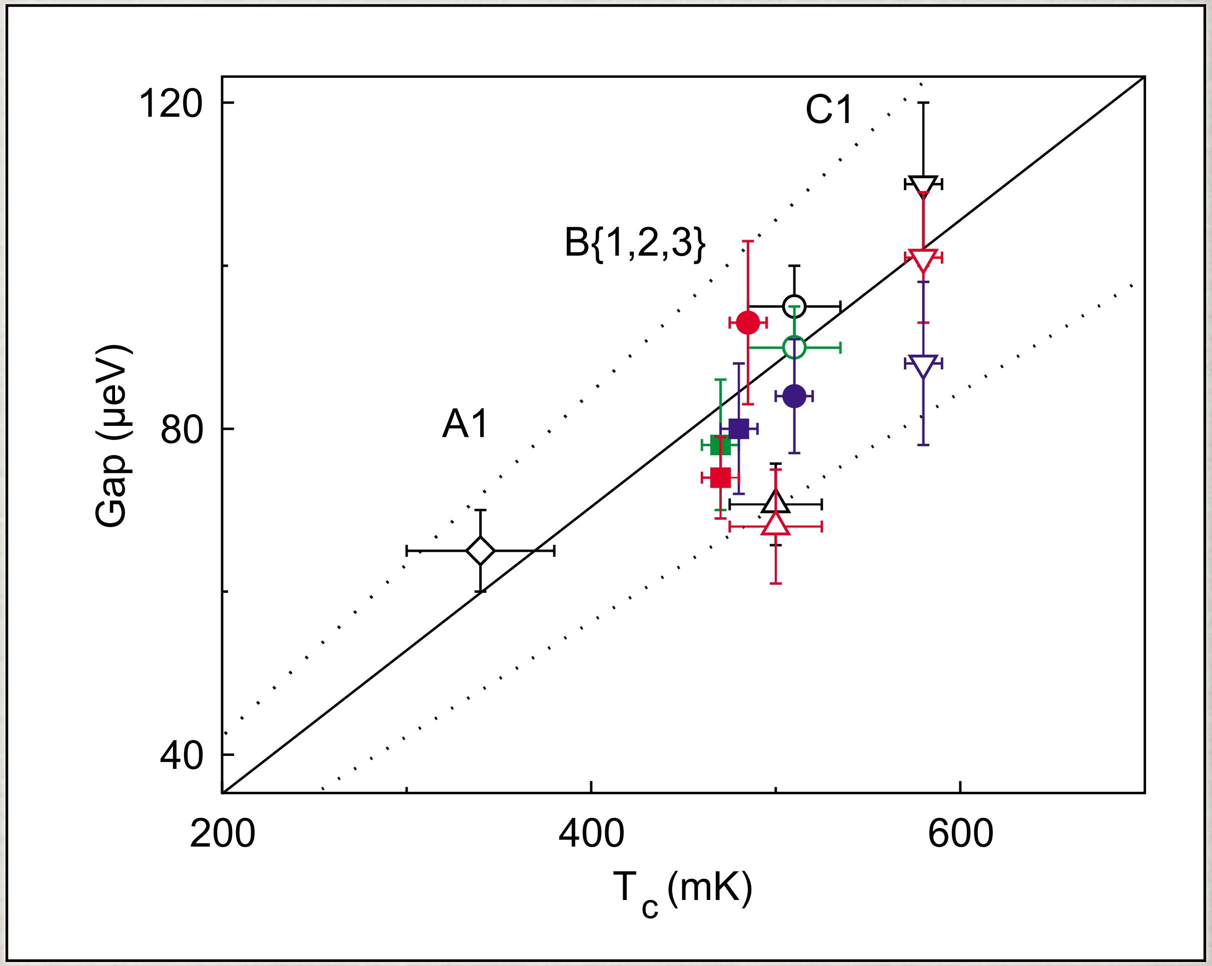
(very flat below 40K)



T_c shifted up 0.7K

(incomplete transition below ~2.5 at-%)

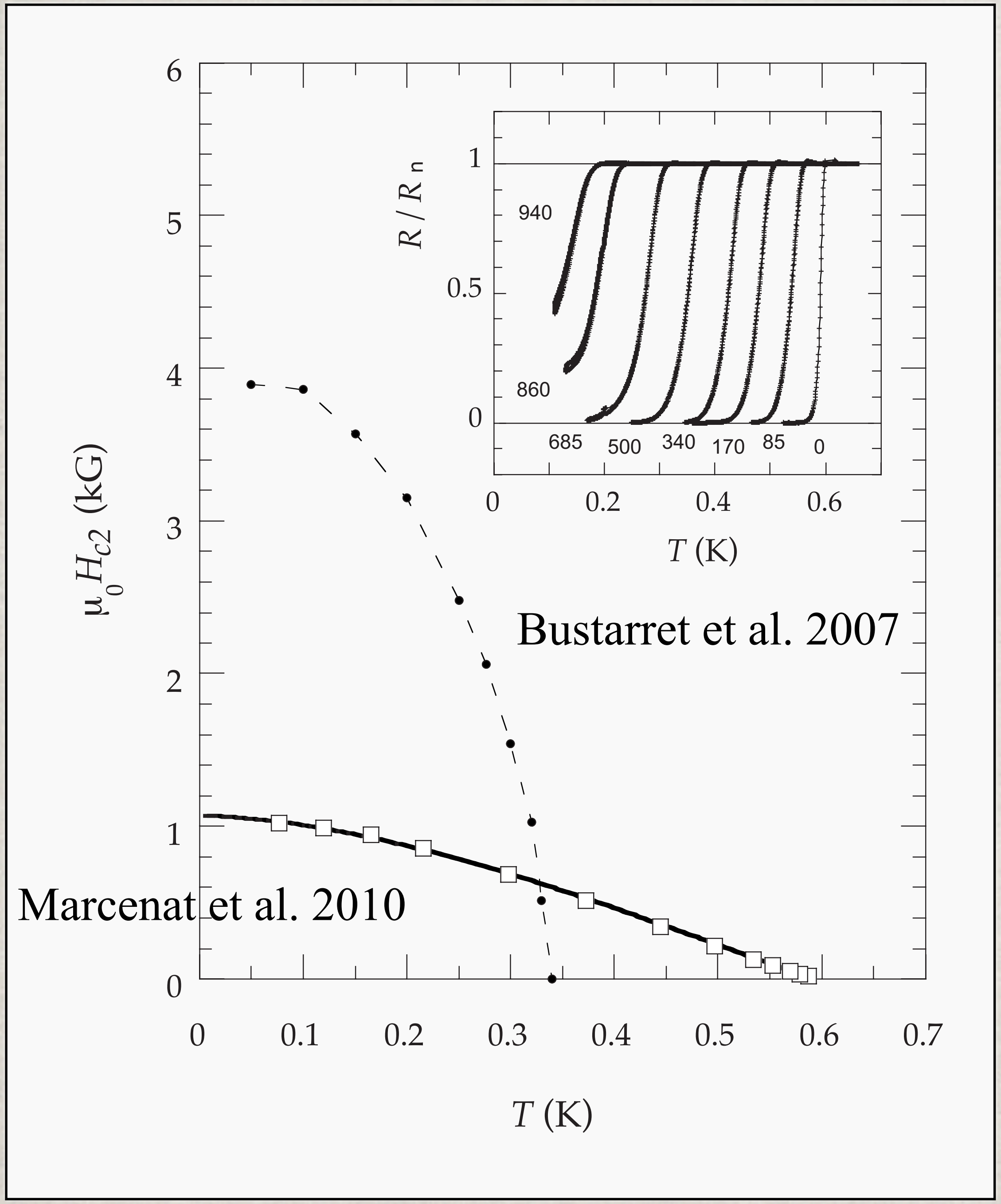




F.Dahlem et al. (2011)

$\Delta/kT_c \sim 1.7$ i.e. close to BCS value

T_c defined at $R/R_n = 0.9$



$H_{c2}(0)$ decreses from 4000G to 1000G in *better* samples

probably type II superconductor eventhough...

$$\xi = \hbar v_F/\pi\Delta \sim 1000 \text{ nm}$$

$$\lambda = \sqrt{m*/\mu_0 e^2 n} \sim 60 \text{ nm}$$

$$\lambda/\xi << 1$$

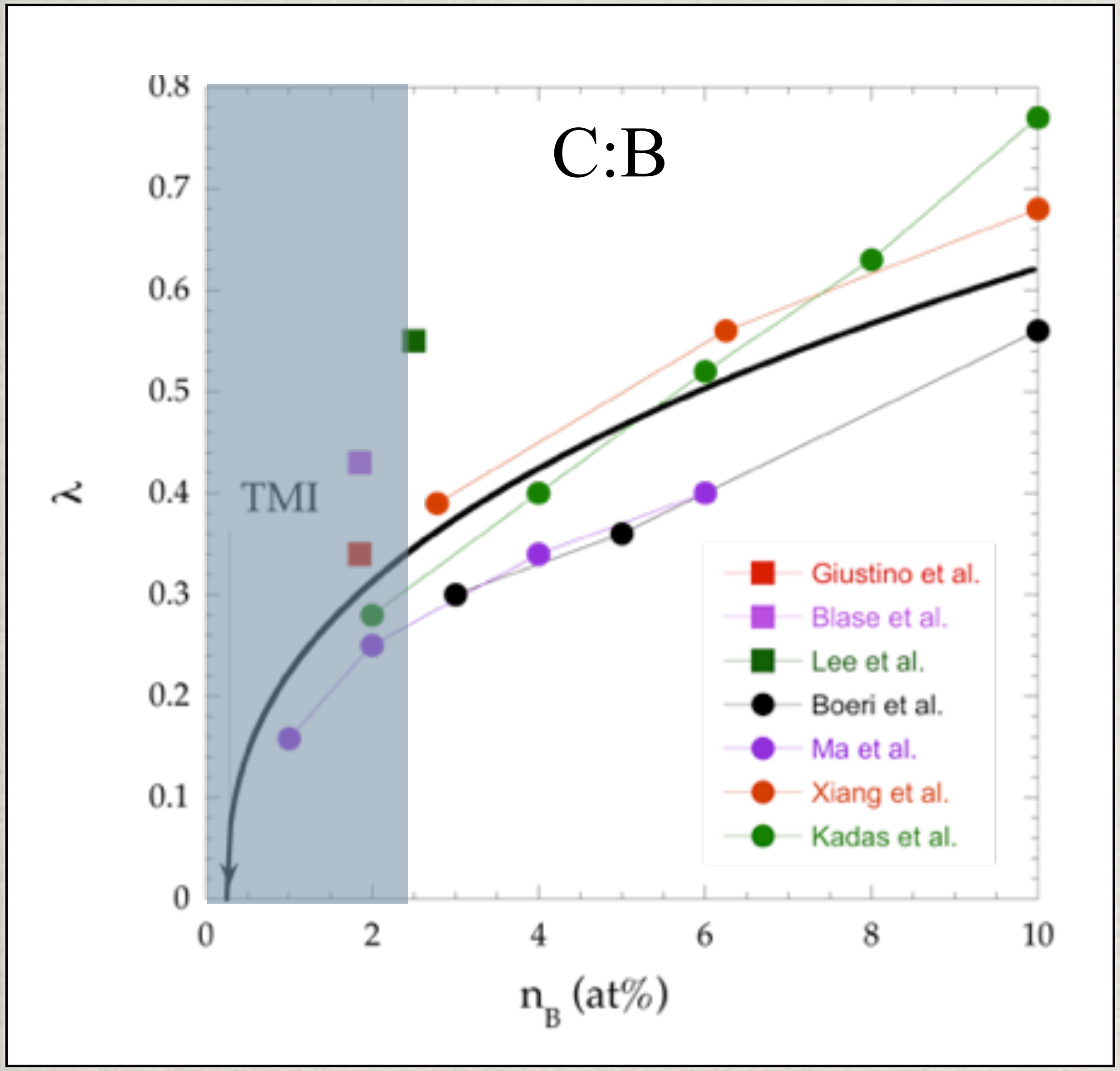
type I superconductivity observed in SiC (Kriener et al. 2008)

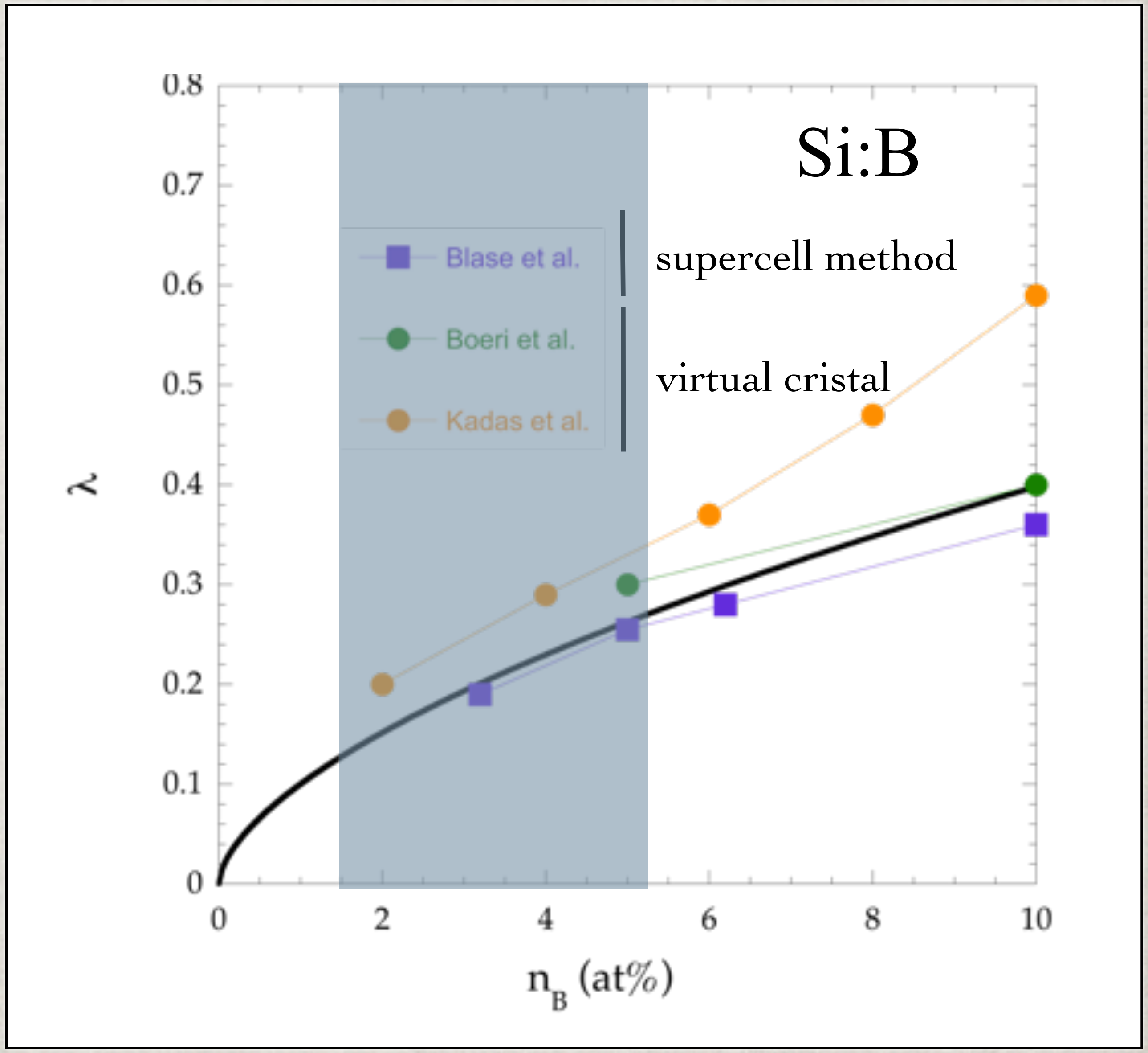
but...

$$l \sim 3 \text{ nm} << \xi$$

DIRTY superconductor

$$\kappa \to 0.7\lambda/l >> 1$$





experimental range
for T_c measurements

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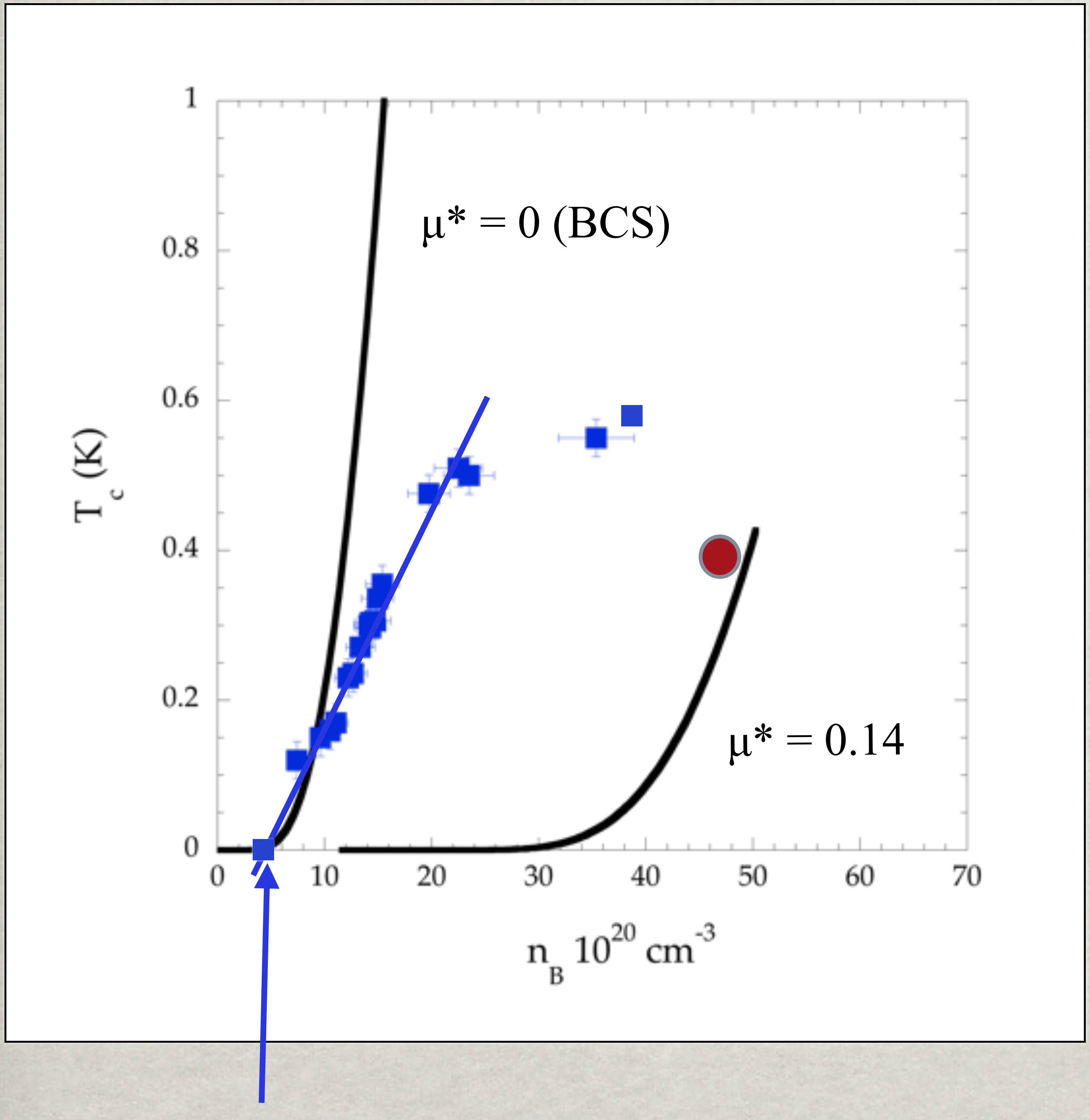
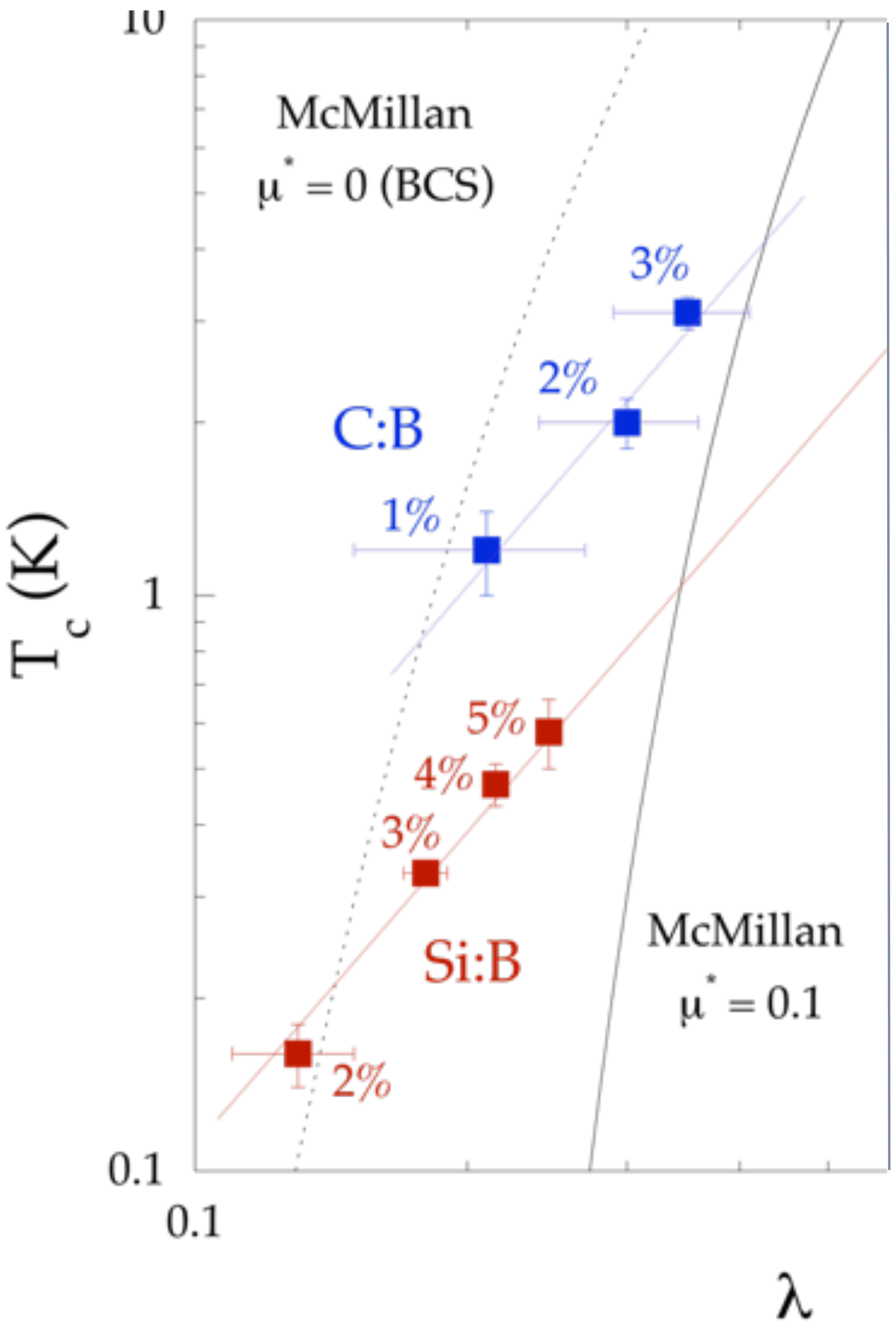


n* ? : NOT related to MIT : $n_c \sim 10^{18}$ cm^{-3}

very reasonable agreement
between calculations and
T_c obtained by Bustarret et al. (2007)
taking $\mu^* \sim 0.14$
standard metal value

but new data (lower n_B values) led to T_c
AGAIN much larger
than calculated values

can NOT be associated with reduced μ^*
$n_B >> n_c$



T_c scales
as λ^α
with α ~ 2 (0.2)

Has this somerthing to do with fractality ?

Feigelman et al. (2007)
Disordered system close to SIT

$$T_c = E_0 \lambda^{1/\gamma} C(\gamma)$$

$$\gamma = 1 - D/3$$

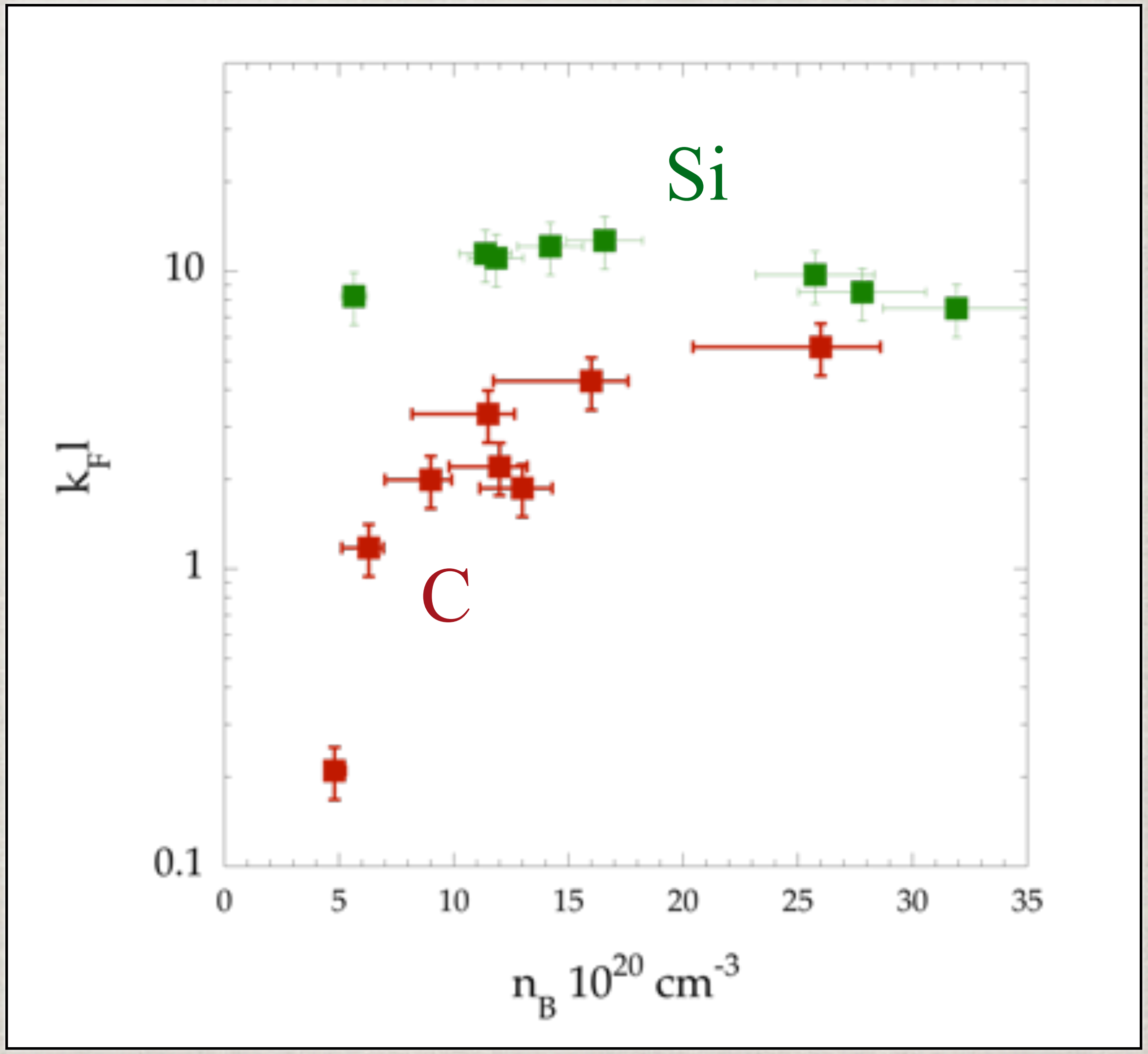
where D is the fractal dimension of eigenstates

numerical calculation
D ~ 1.3
and 1/γ ~ 1.8

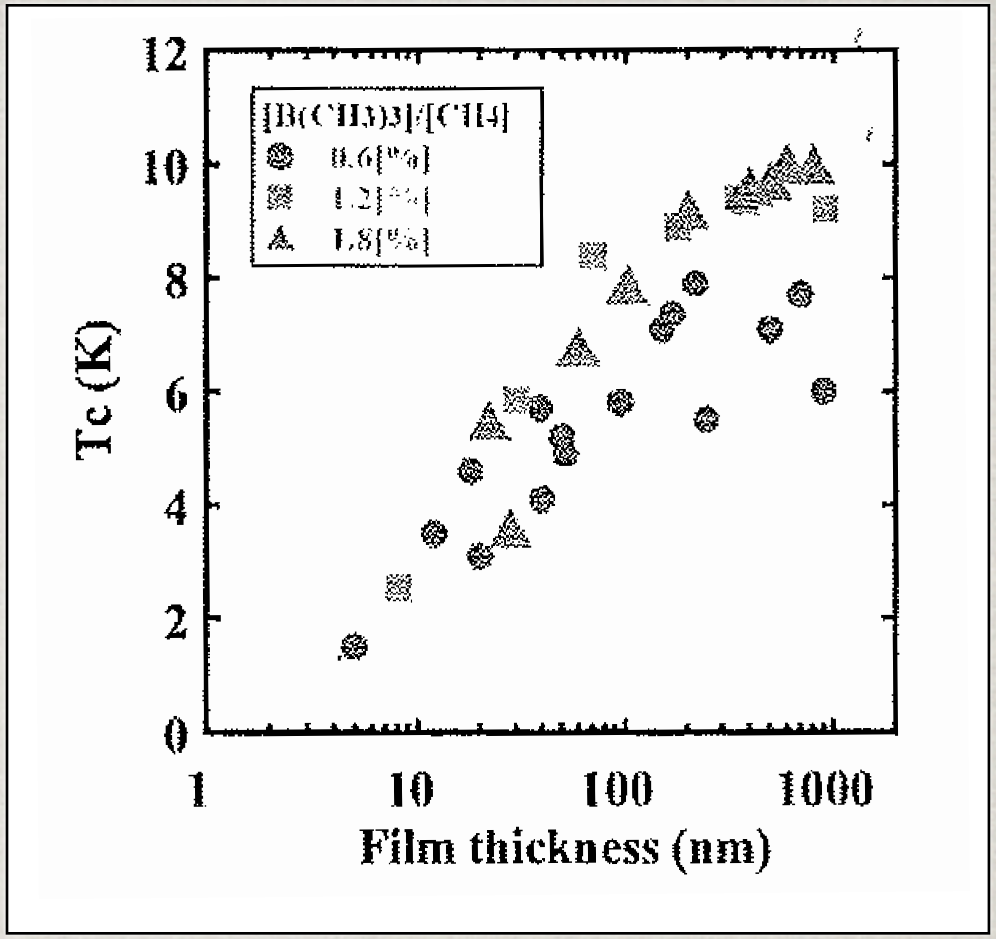
but...

[A] λ calculations made without any disorder nor any strain (induced in the films by substrate)

[B] if $k_F l$ close to 1-3 in C:B
$k_F l \sim 10$ in Si:B

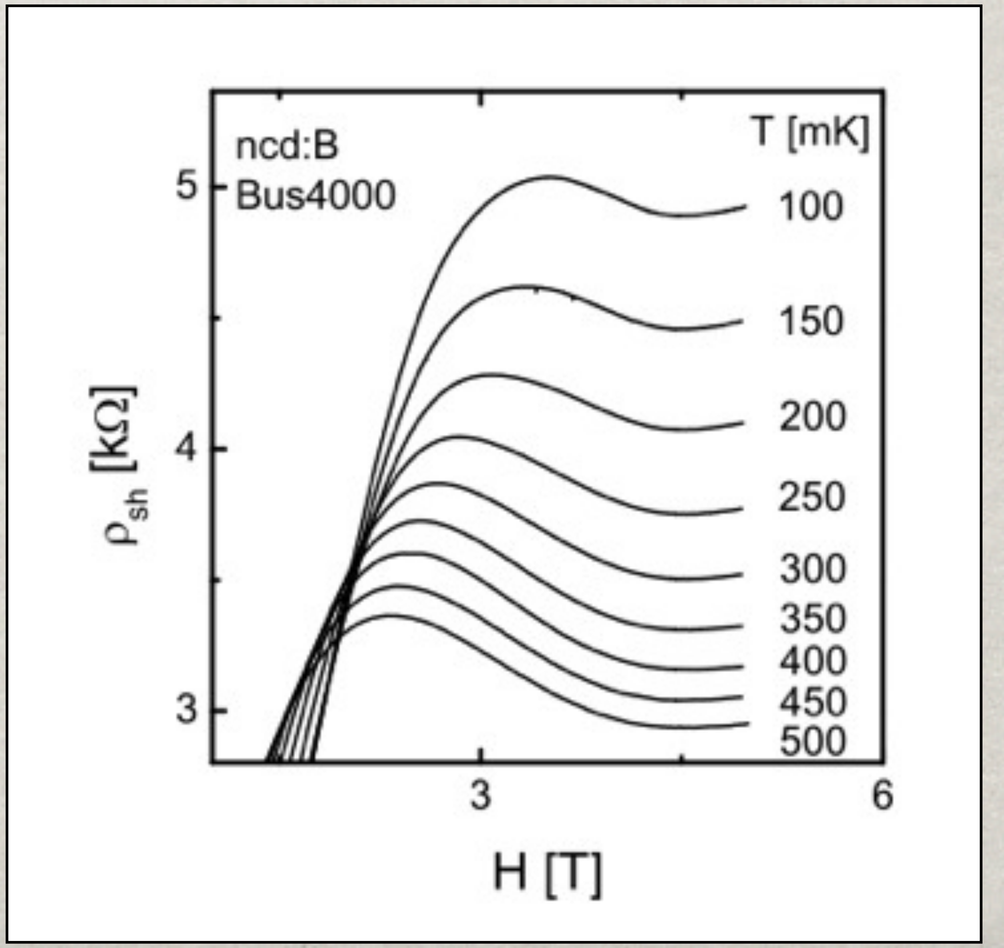


[C] T_c decreses
with the film thickness
in C:B



Kawarada et al. 2011

[D] small MR peak
(T_c = 1K sample B:C nanocrystalites)
but no real «crossing point)



P.Achatz et al. 2008

in Conclusion

- (type II) superconductivity obtained in B doped diamond and silicon films

- T_c remains quite large down to the MIT in C:B $[T_c \sim (n_B/n_c-1)^{0.5}]$

- T_c much larger then expected values deduced from *ab initio* λ calculations in Si:B ($n_B >> n_c$)

- possible λ^2 scaling of T_c in both Si:B and C:B

Thank you for your attention...