Tailoring the crystal structure towards optimal superconductors

Emilia Morosan

Rice University, Houston TX

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OUTLINE

- *“Practical” superconductors*
  - What we know
  - Opportunities for discovery
- *Reduced anisotropy in a new Fe pnictide compound: $CaFe_4As_3$*
- *Interplay between competing interactions*
  - Charge density wave and superconductivity: intercalated dichalcogenides *1T*-Cu_xTiSe_2, *2H*-Cu_xTaS_2
- *Conclusions and outlook*

Acknowledgements

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N. Phuan Ong

“Practical” superconductors

- *High T_c is not enough*
  - More important: high carrier density, low electron mass anisotropy
- *What we know:*

1. Layered crystal structure

Cuprates:

👍 *square Cu-O lattice*

👎 High anisotropy

Pnictides:

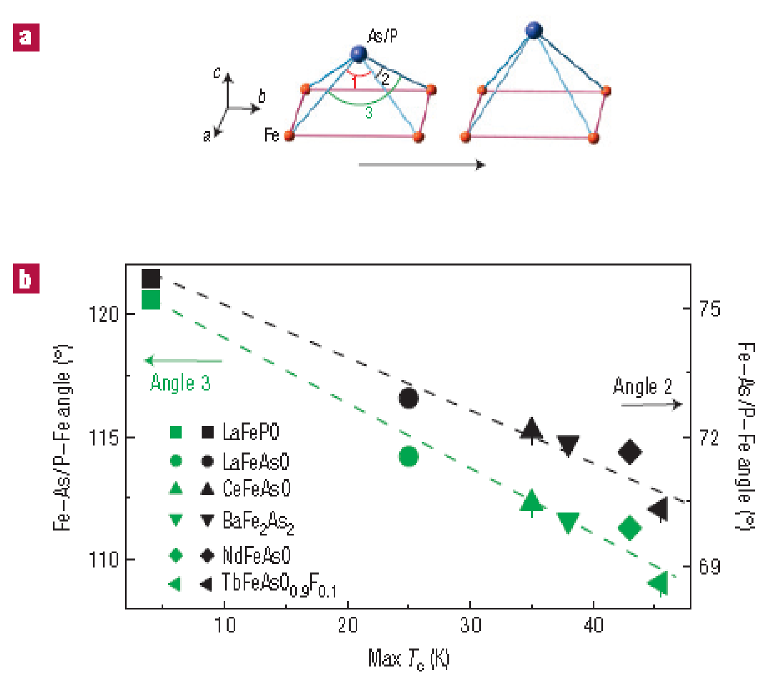
👍 *“perfect” tetrahedra*

👍 *less two-dimensional*

👎 Maximum T_c ~ 50 K

much smaller than maximum in HTS (~160K)

Jun Zhao *et al.* Nature Materials, **7** 953 (2008)



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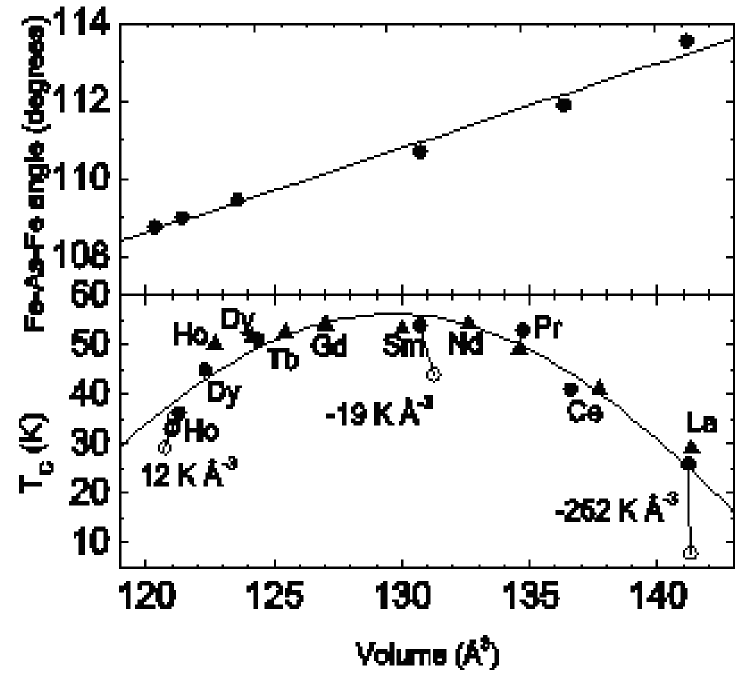
J. Rodgers et al., arxiv 0908.1167 (Aug 11 2009)



“Practical” superconductors

- *What we know:*

  2. Competing interactions: superconductivity and magnetism

  - 👍 *Doping suppresses SDW in favor of SC*
    Fe, Ni “1111”, “122”: $T_c \sim 50$ K

    Kito *et al.*, JPSJ **77** 063707 (2008)

  - 👍 *No magnetic ordering in stoichiometric LiFeAs, $T_c \sim 18$ K*

    Tapp *et al.*, PRB **78** 060505(R) (2008)

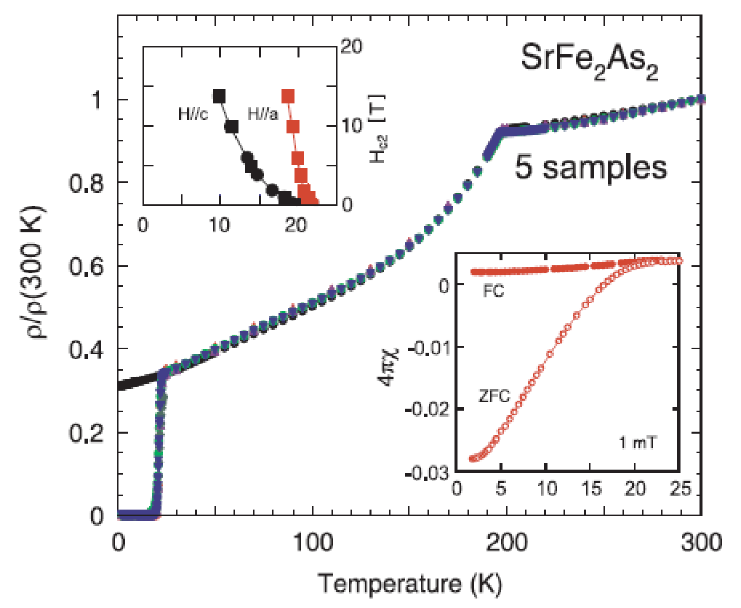
  - 👍 *No magnetic moments in Rh, Ir, Pd, Pt “122” compounds*
    - 👎 Much smaller $T_c \sim$ 1-2 K

    Hirai *et al., JPSJ* ***78*** *023706 (2009);* Berry *et al., PRB* ***79*** *180502(R) (2009)*

“Practical” superconductors

- *What we know:*
  2. **Competing interactions:** superconductivity and magnetism

Saha *et al.*, PRL **103** 037005 (2009)



👍 *Coexistence of magnetic order and SC?*

Strain-induced SC and FM in stoichiometric SrFe$_2$As$_2$

👍 Partial superconducting transitions in stoichiometric “122” compounds

👎 *Sample-dependent*

Tanatar *et al., PRB **79** 134528 (2009);* Torikachvili *et al., PRL 101 057006 (2009);*
Torikachvili *et al., PRB 80 014521 (2009)*

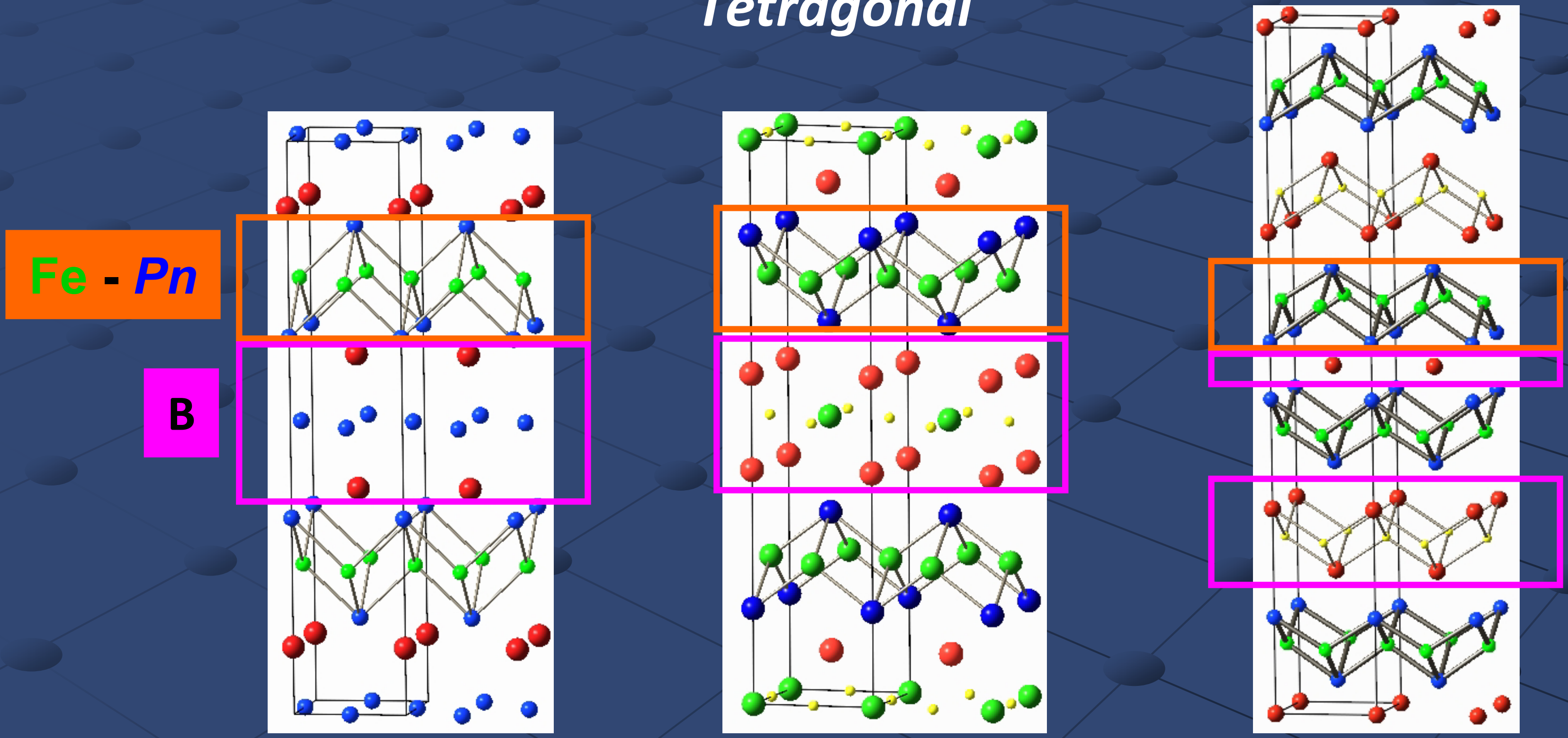
“Practical” superconductors

- *Opportunities for discovery:* interplay of layered structures and competing interactions
  - Superconducting “Fe-As” type layers separated by blocking layers (B)
    - *B = R-O (“1111”), A^{2+} (“122”), A^{1+} (“111”)*
  - Beyond pnictides: $Fe_{1+\delta}Se$
    - *no blocking layer*

Opportunities for discovery

- *Design potential new SC: “Fe-As” + B*

Tetragonal

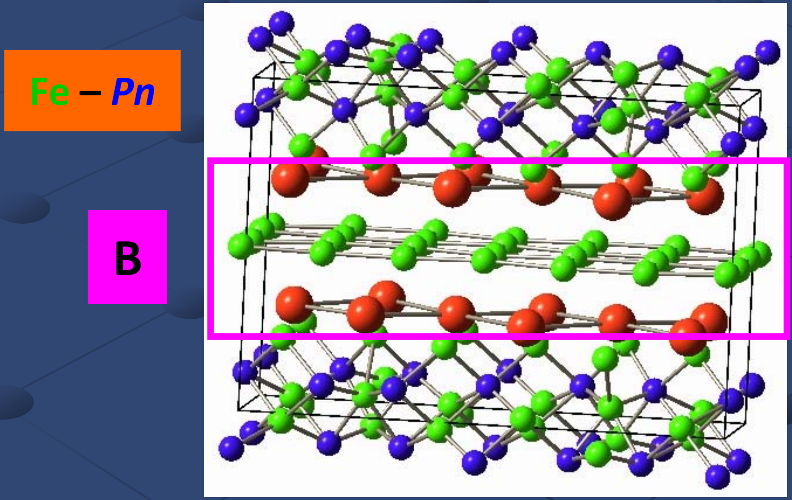


Opportunities for discovery

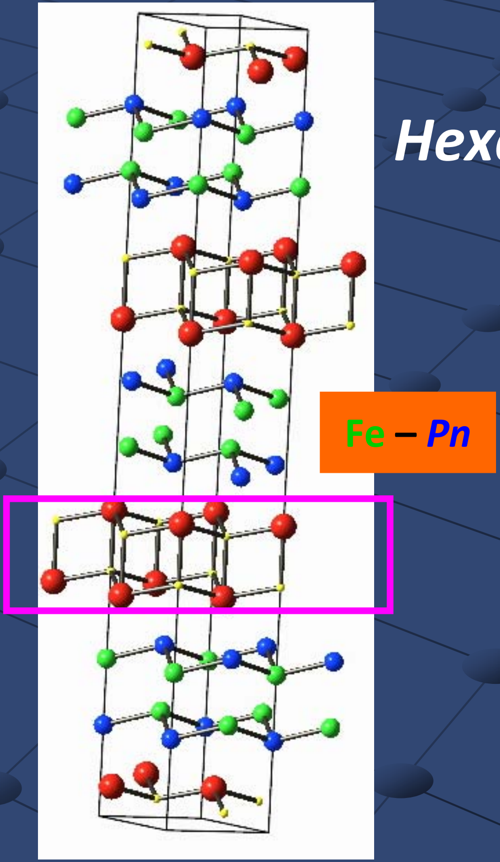
- *Design potential new SC: “Fe-As” + B*

Will lower symmetry work?

Orthorhombic



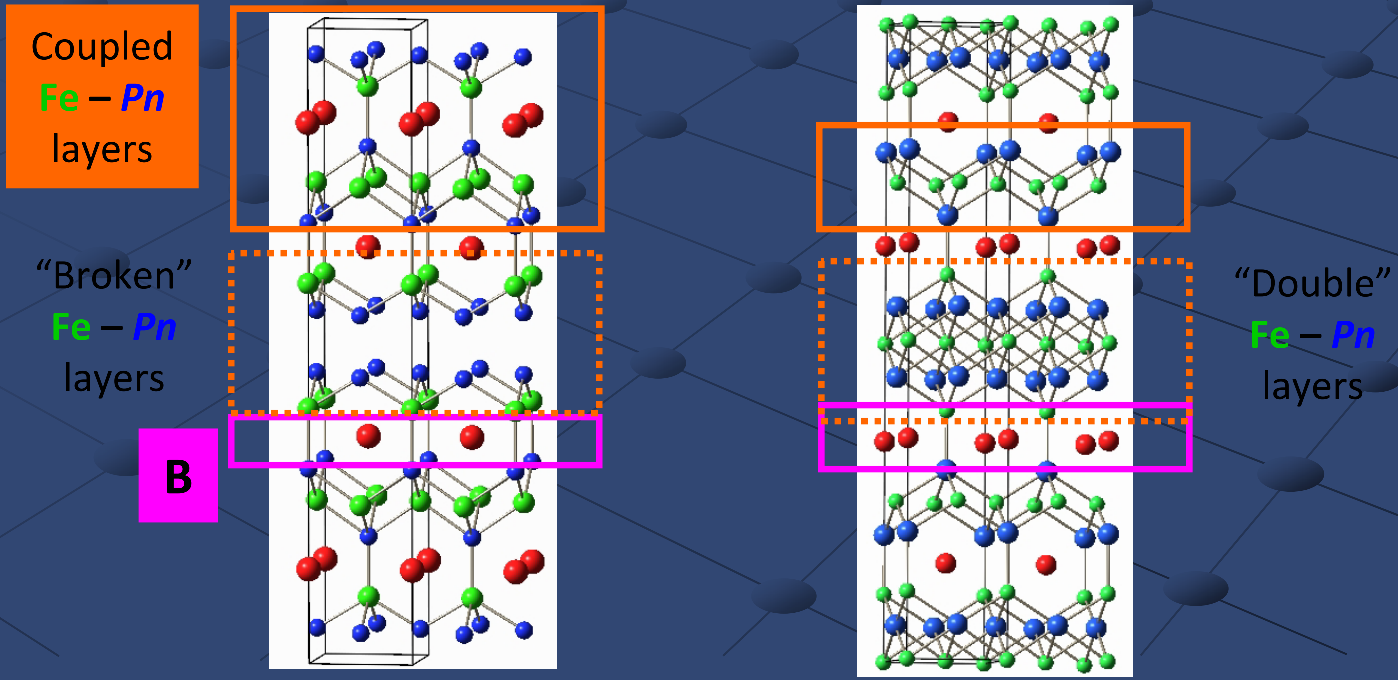
Hexagonal



Opportunities for discovery

- *Routes to reduced anisotropy:*
  - pressure: push layers together
  - doping = chemical pressure
  - coupled Fe-*Pn* layers $\Rightarrow$ less 2D crystal structure?

Tetragonal



Coupled **Fe – *Pn*** layers

“Broken” **Fe – *Pn*** layers

B

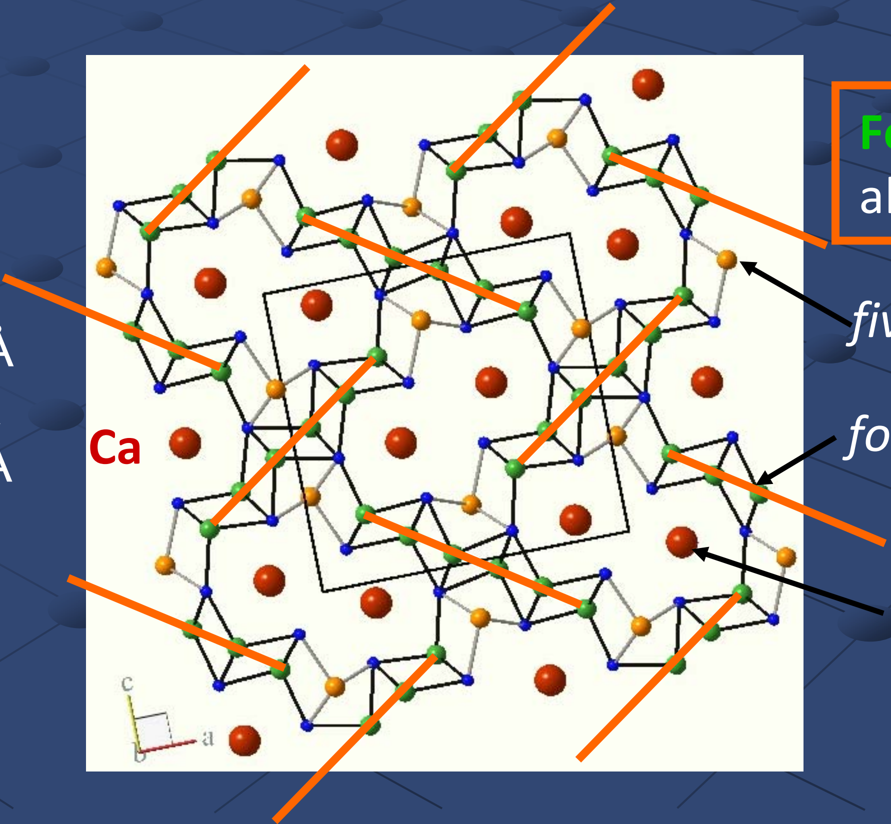
“Double” **Fe – *Pn*** layers

Opportunities for discovery

- *Routes to reduced anisotropy:*
  - "locally layered" structure: **$\mathbf{CaFe_4As_3}$**

Zhao *et al.,* PRB **80** 020404(R) (2009)
Todorov et al., JACS **131** 5405 (2009)

Orthorhombic
P*nma*
a = 11.88407 Å
b = 3.73422 Å
c = 11.58577 Å



Fe-As ribbons form channels along b axis

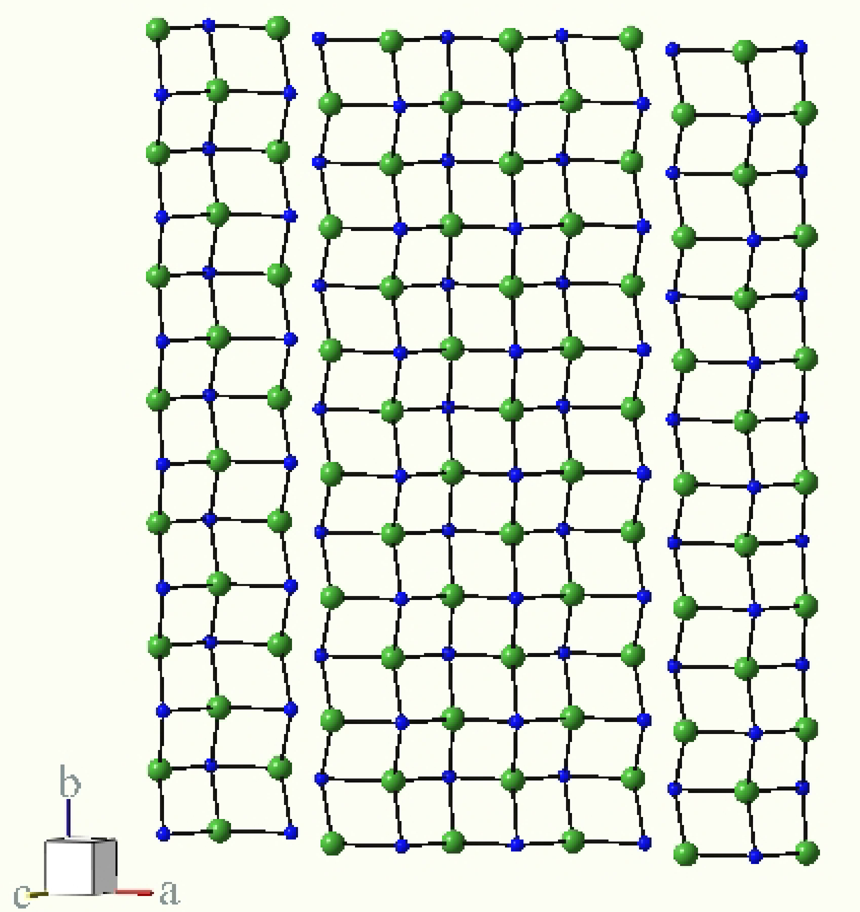
five fold coordinated Fe

four fold coordinated Fe

Ca ions sit in channel

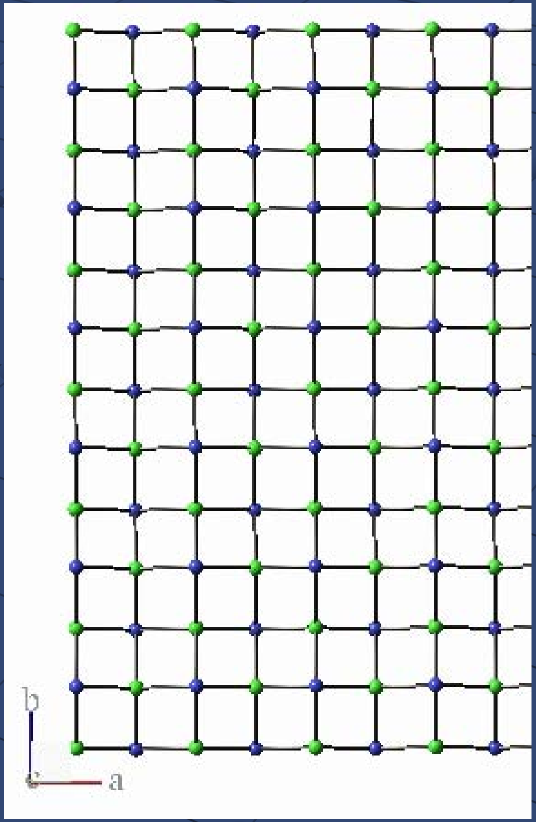
$CaFe_4As_3$ – crystal structure

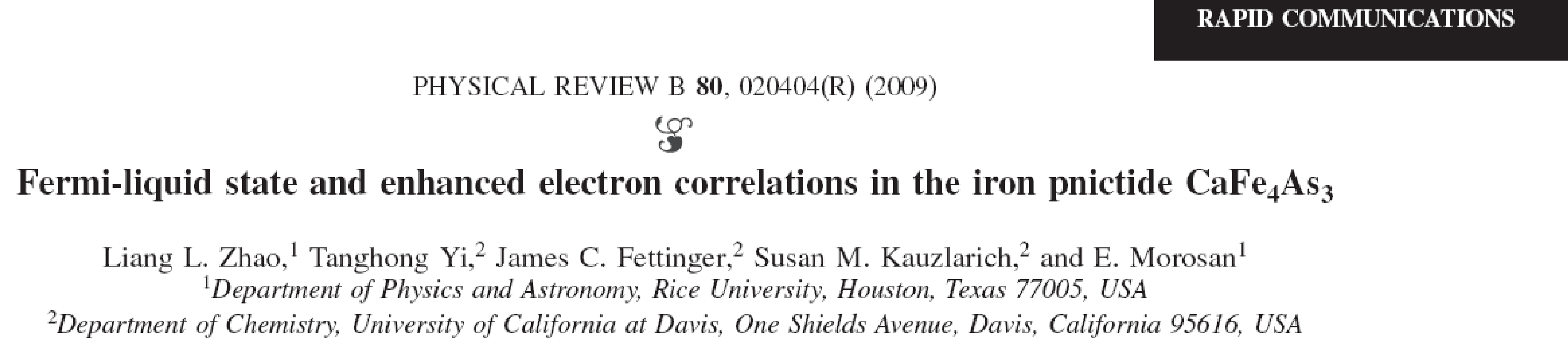
- *Infinitely long, narrow Fe-As ribbons*



LaFeAsO

Infinite Fe-As planes





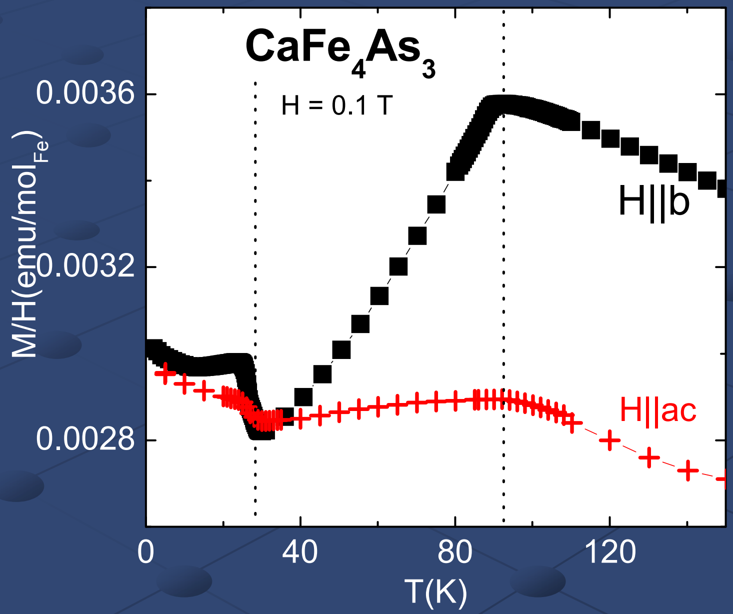
RAPID COMMUNICATIONS

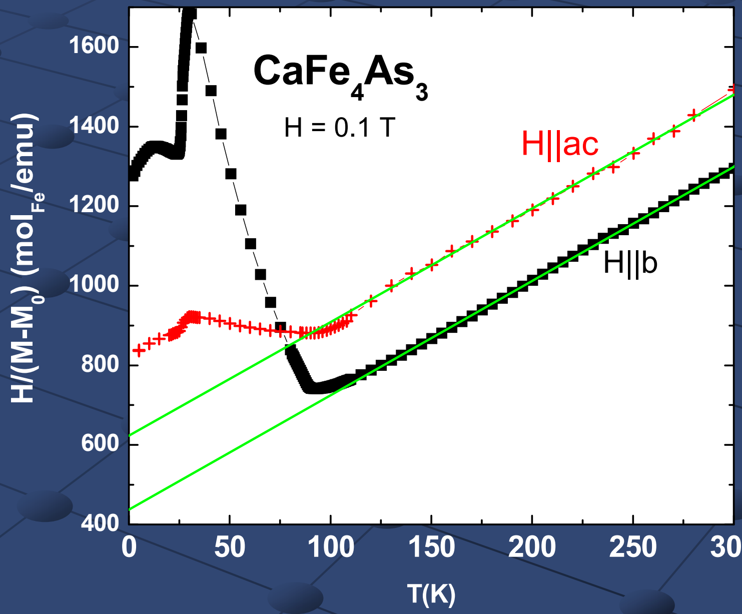
PHYSICAL REVIEW B **80**, 020404(R) (2009)

Fermi-liquid state and enhanced electron correlations in the iron pnictide $CaFe_4As_3$

Liang L. Zhao,[1] Tanghong Yi,[2] James C. Fettinger,[2] Susan M. Kauzlarich,[2] and E. Morosan[1]
[1]*Department of Physics and Astronomy, Rice University, Houston, Texas 77005, USA*
[2]*Department of Chemistry, University of California at Davis, One Shields Avenue, Davis, California 95616, USA*

- *M(T) H = 0.1 T*





Curie-Weiss behavior at high T:

$\chi(T) = \chi_0 + C/(T - \theta)$

$\chi_0 \sim 10^{-3}$ emu/mol$_{Fe}$

$\mu_{eff} = 1.7\ \mu_B$

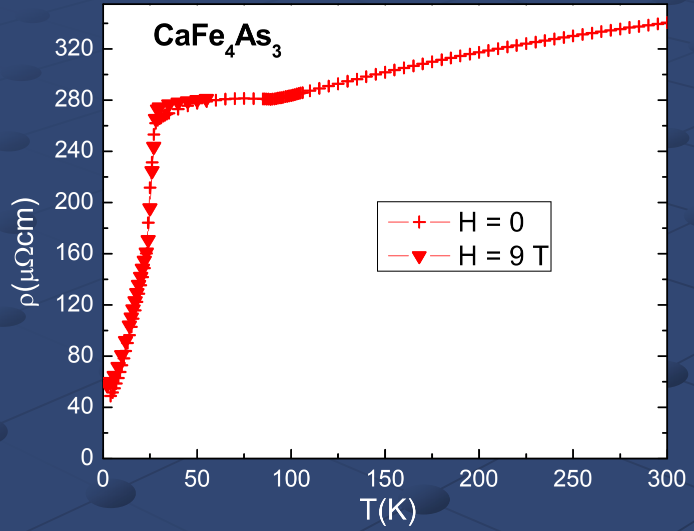
Magnetic ordering (antiferromagnetic) $T_N = 88$ K

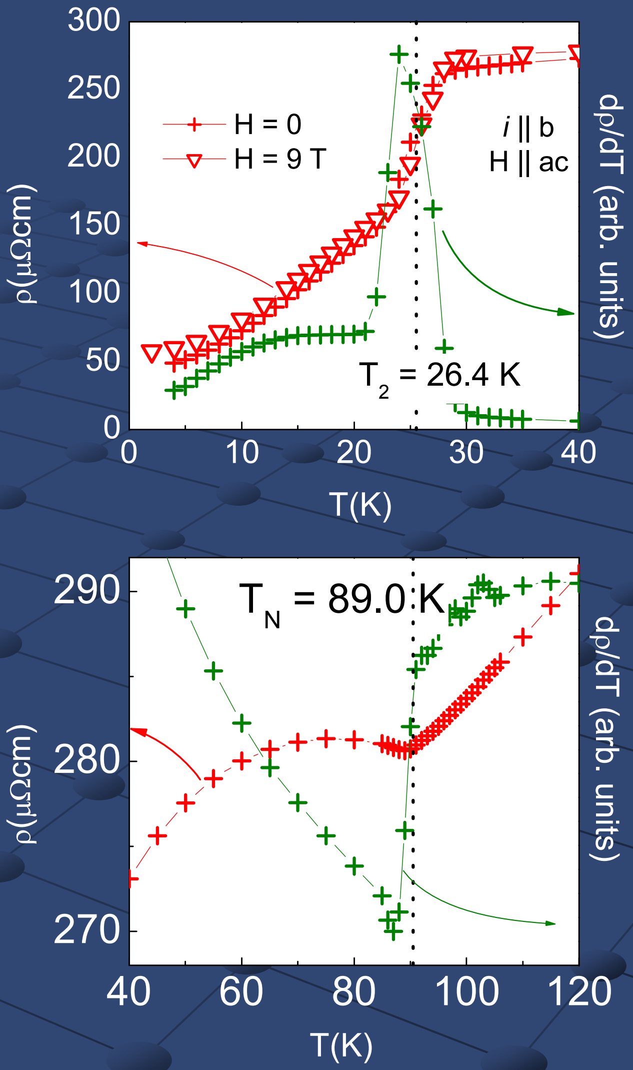
Second phase transition around $T_2 = 26$ K

Slight upturn in low-T M(T) $\Rightarrow$ FM ?

$CaFe_4As_3$ – resistivity

- $\rho(T)$ $i||b$





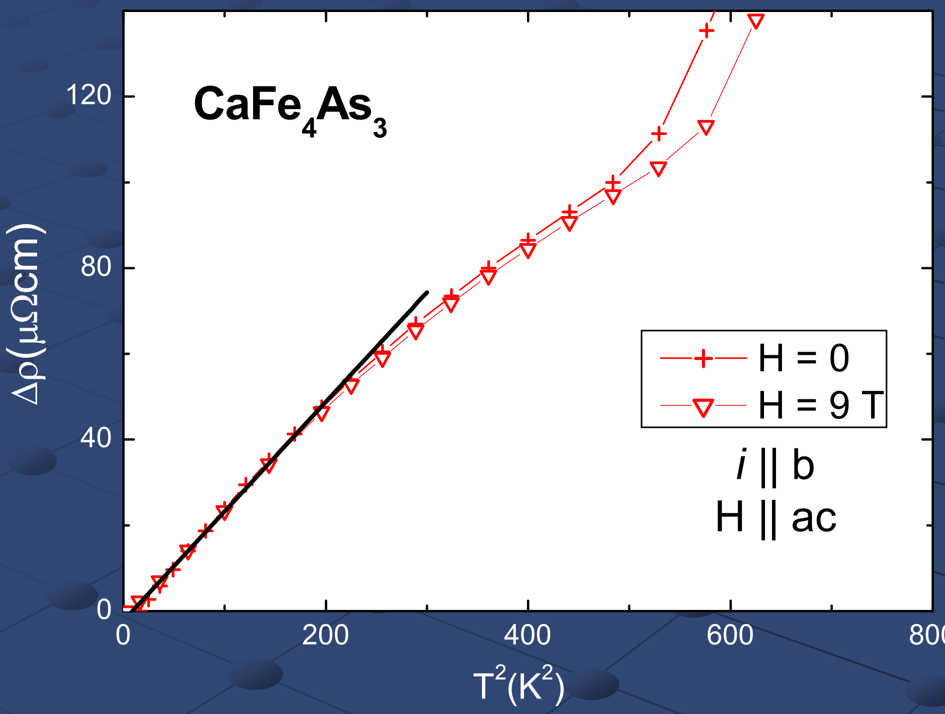
Metallic above T_N = 89 K

Local minimum around $T_N \Rightarrow$ SDW

Second phase transition around T_2 = 26 K

$CaFe_4As_3$ – Fermi liquid behavior at low T

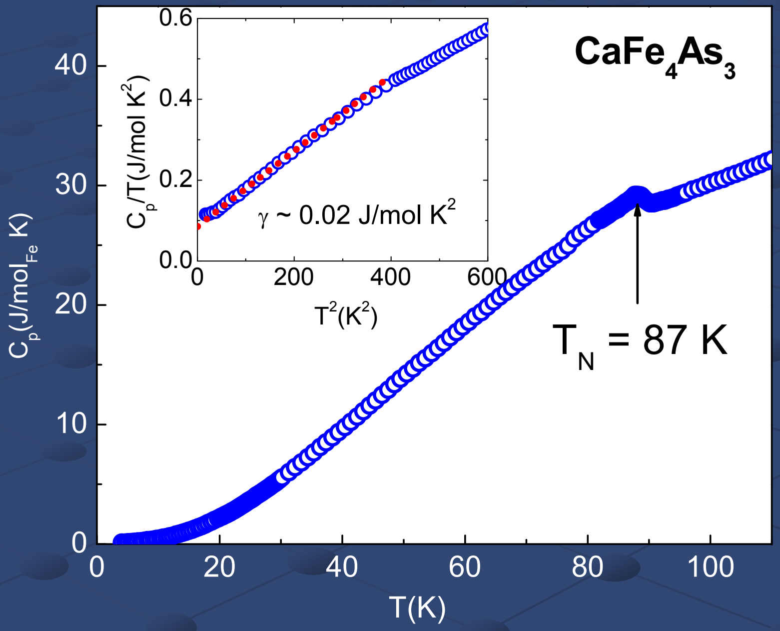
- *ρ(T)* *i*||b

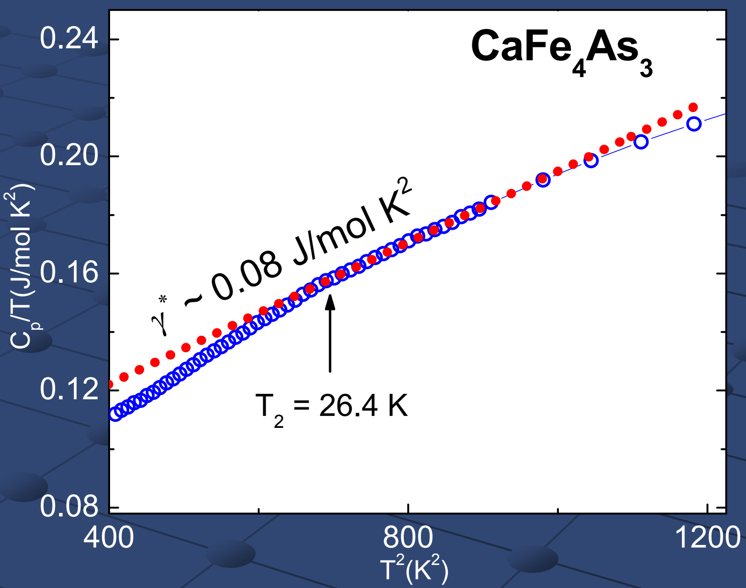


ρ_0 = 42 μΩ cm

$\Delta\rho \sim AT^2$, A = 0.25 μΩ cm/K^2

$CaFe_4As_3$ – specific heat

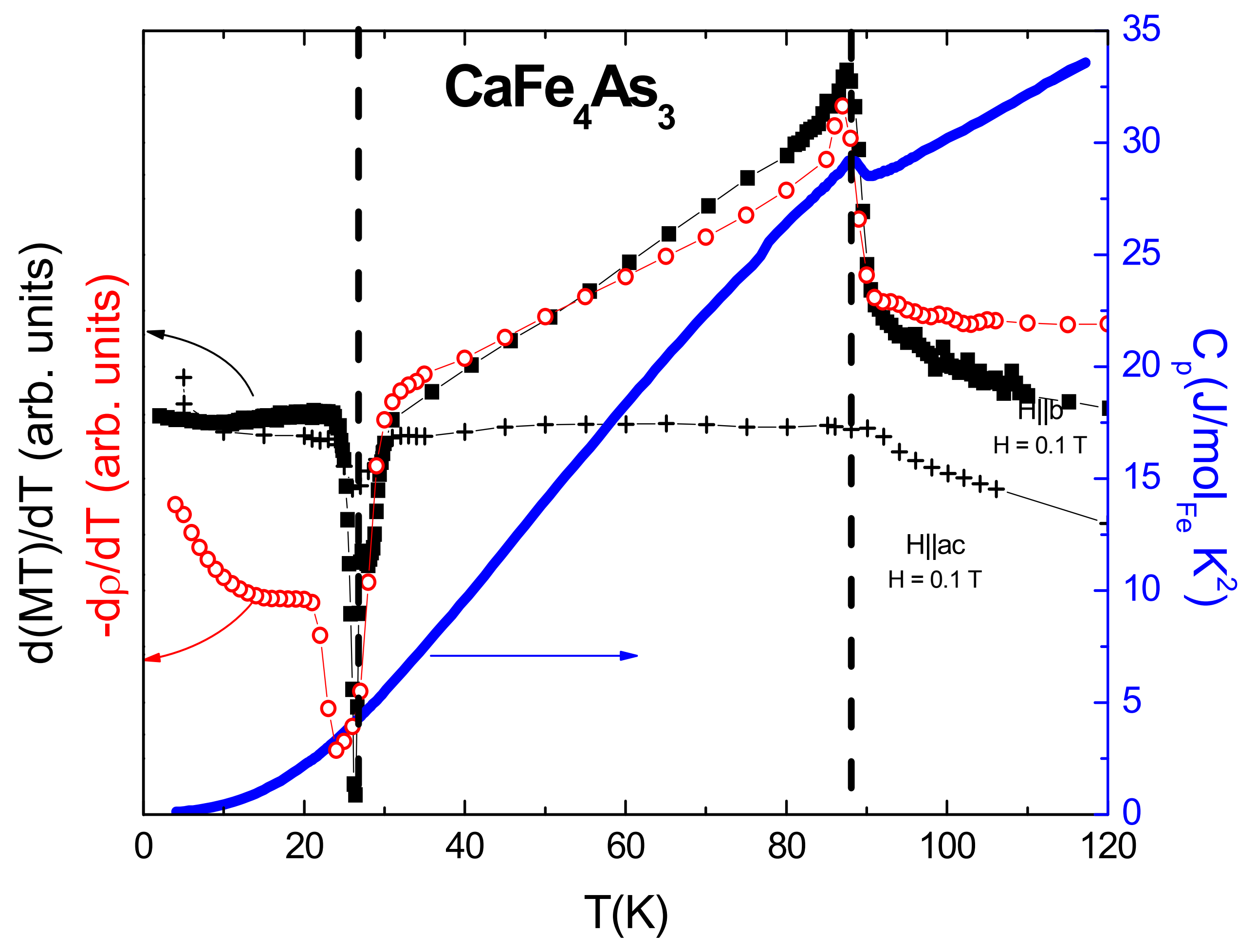




- Peak at T_N but no visible feature around low-T transition in C_p
- $\gamma = 20\ mJ/(mol_{Fe}\ K^2)$

- Linear $C_p/T\ (T^2)$ above T_2
- High temperature (26 K < T < 36 K) $\gamma^* = 20\ mJ/(mol_{Fe}\ K^2)$

$CaFe_4As_3$


$CaFe_4As_3$
d(MT)/dT (arb. units)
-dρ/dT (arb. units)
C_p (J/mol$_{Fe}$ K^2)
T(K)
0
20
40
60
80
100
120
0
5
10
15
20
25
30
35
H||b
H = 0.1 T
H||ac
H = 0.1 T

$CaFe_4As_3$ – Kadowaki-Woods ratio

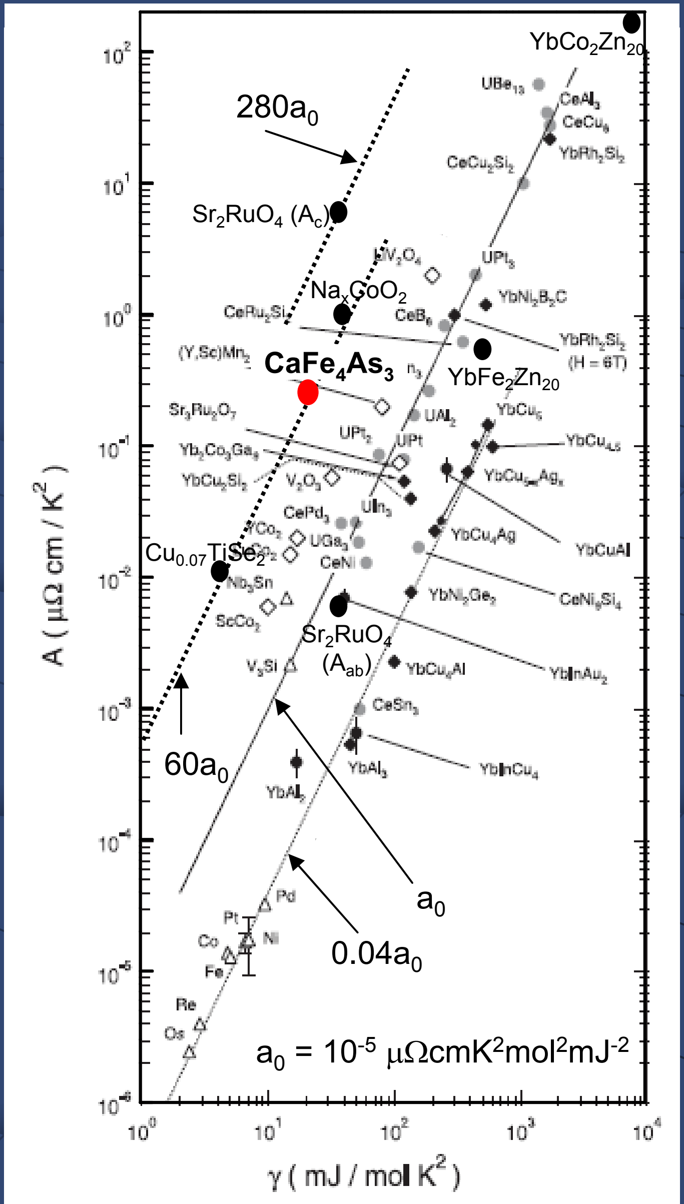
0 < T < 15 K:

- Electronic specific heat coefficient
  - $\gamma \sim 20$ mJ/(mol$_{Fe}$ K^2)
- Fermi liquid behavior:
  - $\Delta\rho \sim AT^2$, $A = 0.25\ \mu\Omega$ cm/K^2

$$\Downarrow$$

$$KW = A/\gamma^2 = 55\ a_0$$

$$(a_0 = 10^{-5}\ \mu\Omega \text{ cm mol}^2\text{ K}^2/\text{ mJ}^2)$$

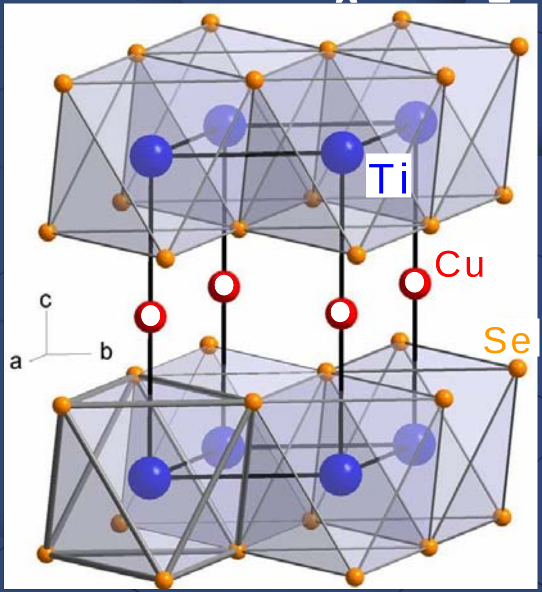


$CaFe_4As_3$ - next steps

- Doping and pressure studies
- Can SC be induced in this 3D “locally” layered structure?
- Is there FM coupling at low T?

“Practical” superconductors

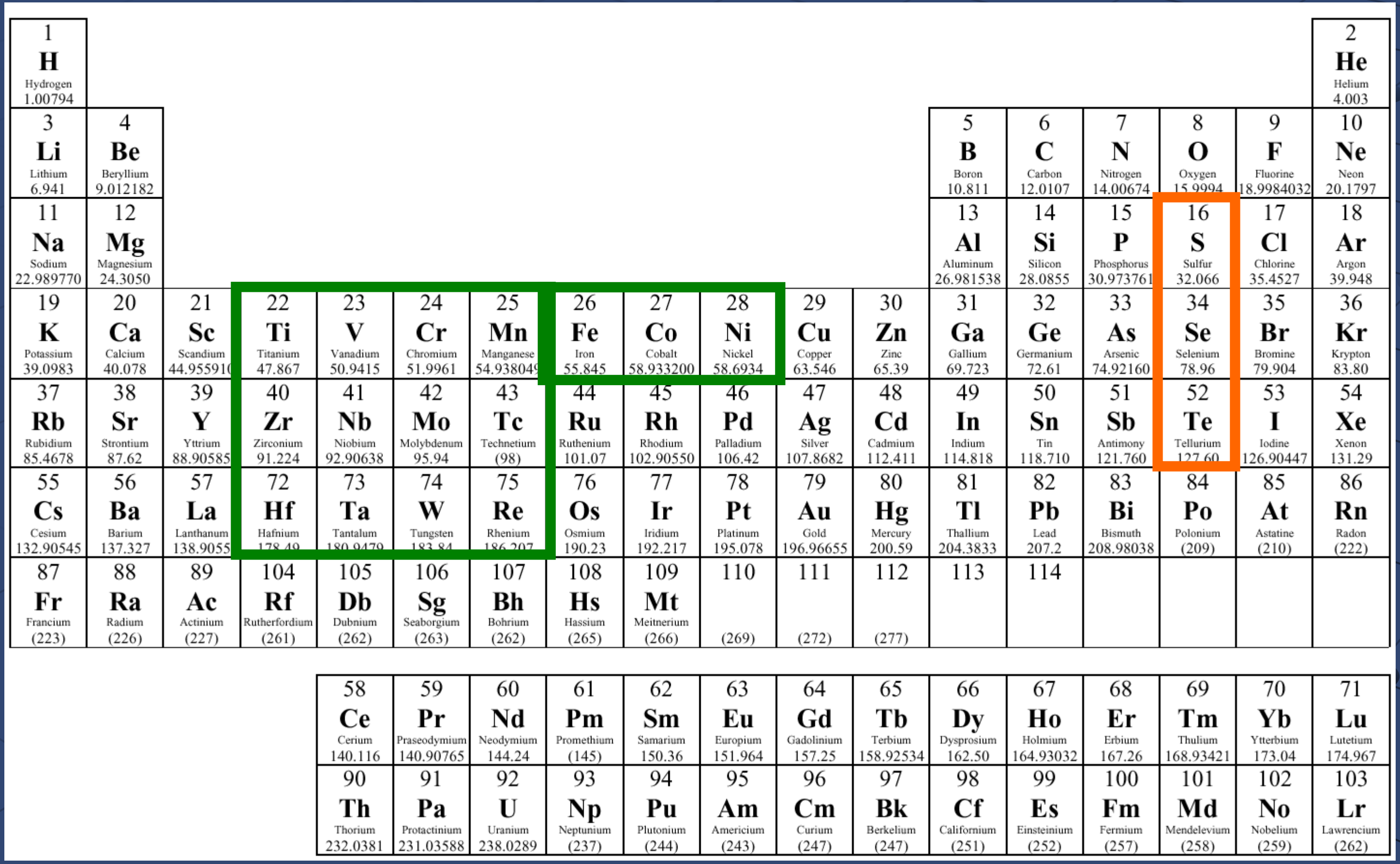
- *What we know:*
  1. Layered crystal structure
     - *Reduced anisotropy: $CaFe_4As_3$*
  2. **Competing interactions: charge density wave and superconductivity – Cu_xTiSe_2**



CDW-to-SC transition in Cu_xTiSe_2

- *Layered dichalcogenides (S, Se, Te based compounds)*

M = transition metal **X = S, Se, Te**



1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.95591	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				
				58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
				90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

CDW-to-SC transition in Cu_xTiSe_2

- *Layered dichalcogenides (S, Se, Te based compounds)*
  - Often display spin density wave, charge density wave transitions
  - Interesting physics, ground states can be tuned between different ground states
    - magnetic field
    - chemical doping
    - pressure

CDW-to-SC transition in Cu_xTiSe_2

- CDW and superconductivity: competing collective electron states

- Tuning parameters (pressure, doping) used to study this competition in low-dimensional systems where both states existed

- No known system where chemical doping results in new superconducting state

- Cu_xTiSe_2: first example of doping induced CDW-to-superconductivity transition

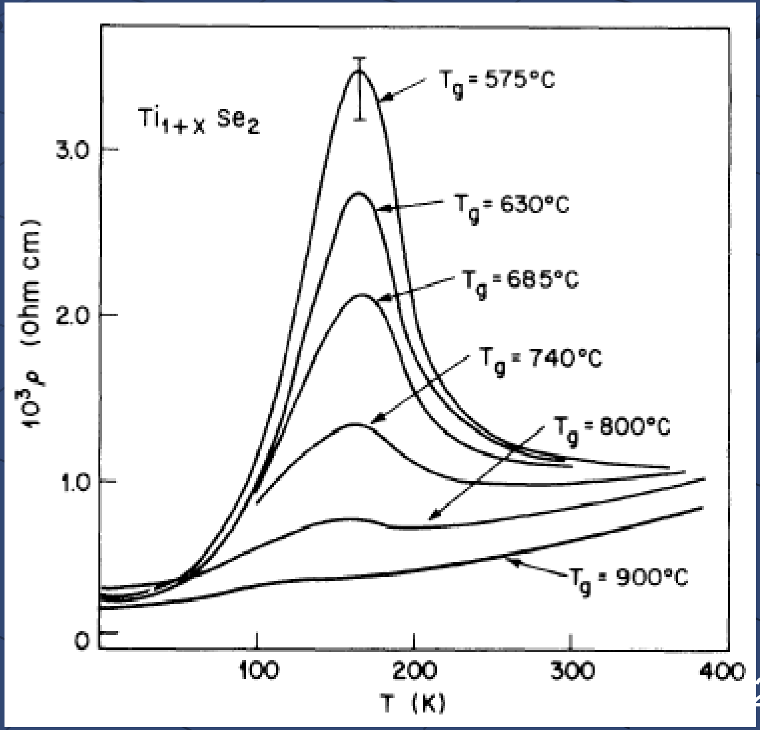
Properties of $TiSe_2$

- *Layered (2D) dichalcogenide*
- *Charge density wave (CDW) transition: $T_{CDW} \approx 200$ K*
- *No incommensurate CDW*
- *Mechanism for the CDW formation – controversial*

- Not driven by Fermi surface nesting
- Exciton formation, indirect Jahn-Teller effect

- Resistivity very sensitive to non-stoichiometry and impurities

DiSalvo *et al., Phys. Rev. B* **14** (1976)



Properties of pure $TiSe_2$

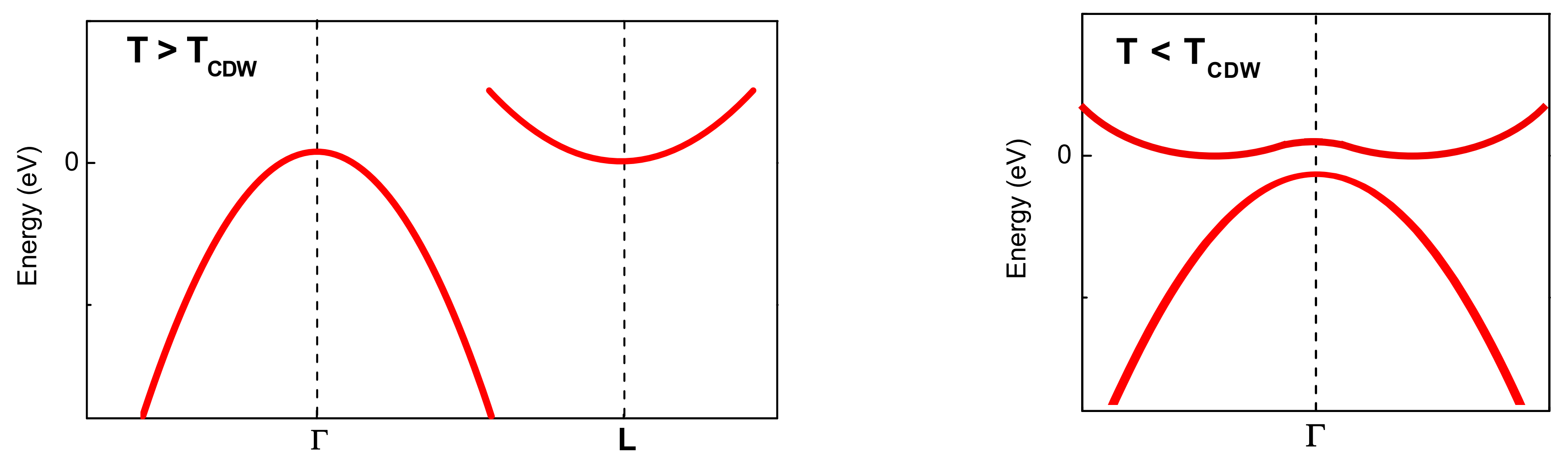
Normal state ($T > T_{CDW}$): Semimetal or semiconductor ?

$T > T_{CDW}$

- small indirect gap

$T < T_{CDW}$

- Folding of L point at Γ
- Larger indirect gap at different location in the Brillouin zone



Properties of pure $TiSe_2$

Normal state: Semimetal or semiconductor ?

DiSalvo et al., Phys. Rev. B *14 (1976)*

Bachrach and Skibowski, Phys. Rev. Lett. *37 (1976)*

Friend et al., *J.* Phys *C:* Solid State Phys. *10 (1977)*

Wilson, Solid State Commun. *22 (1977)*

Zunger,A. and A.J. Freeman, Phys. Rev. B *17 (1978)*

Chen et al., Phys. Rev. B *21 (1980)*

Margaritondo et al., Phys. Rev. B *23 (1981)*

H. Myron and A. Freeman, Phys. Rev. B *9 (1974)*

Stoffel et al., Phys. Rev. B *31 (1985)*

Anderson et al., Phys. Rev. Lett. *55 (1985)*

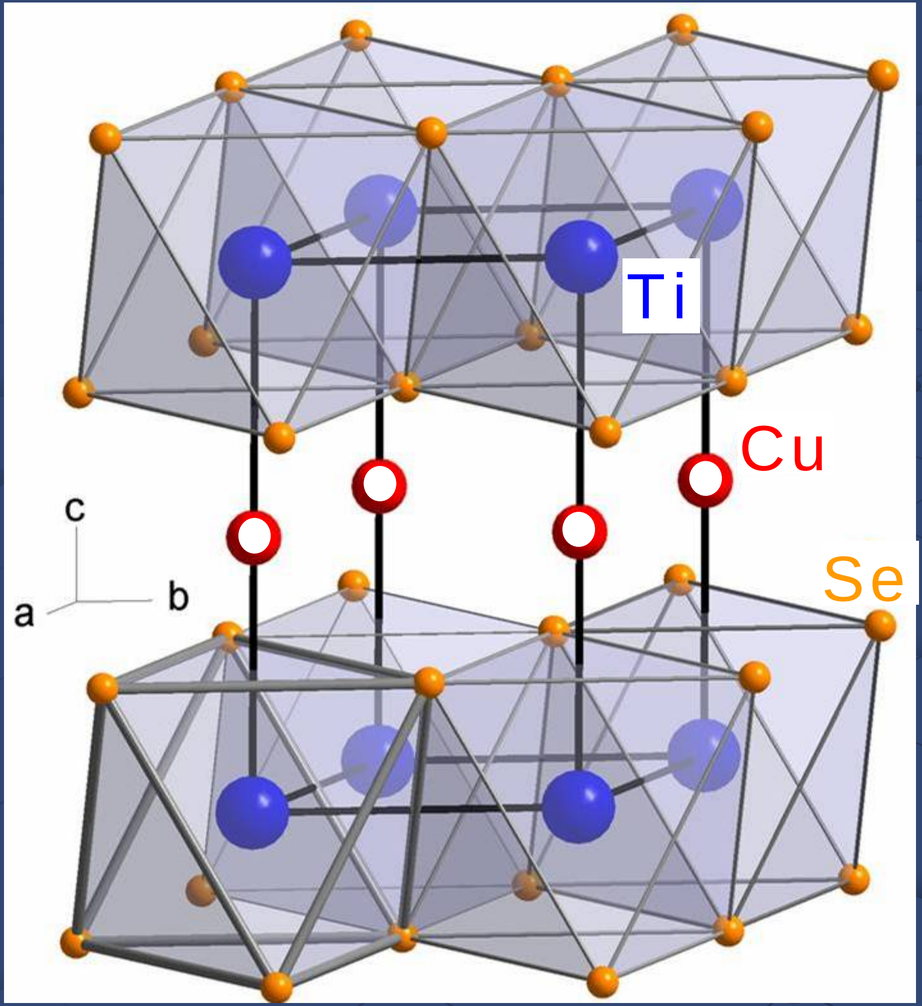
Starnberg et al., *J.* Phys *C:* Solid State Phys. *20 (1987)*

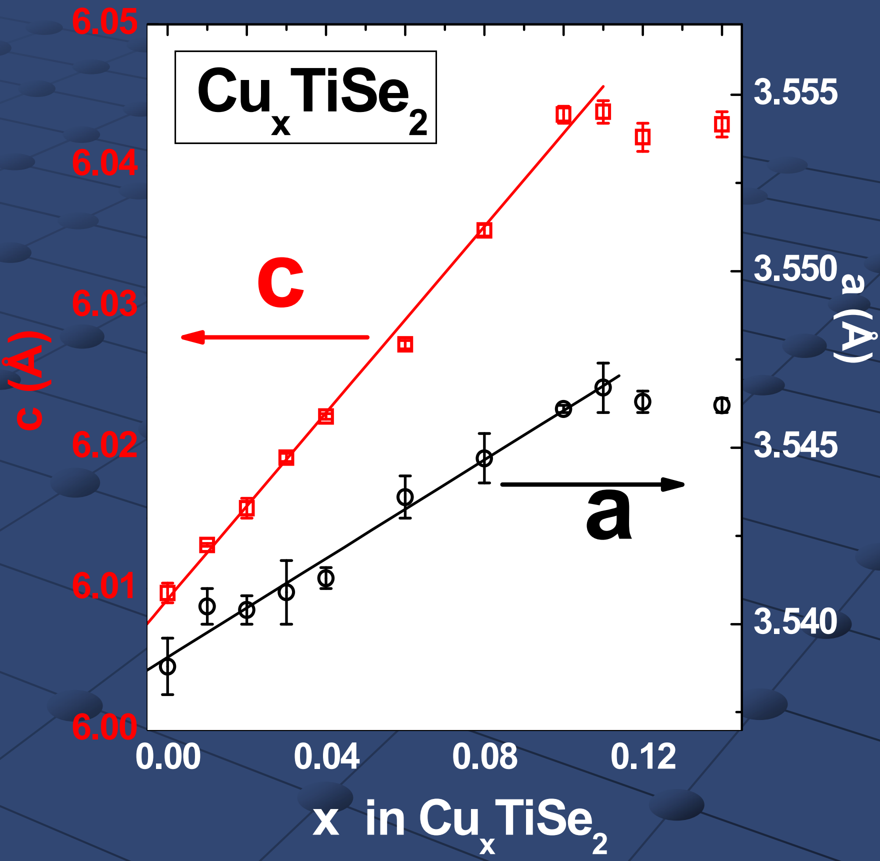
R. Coleman et al., Surface Properties of Layered Structures *(1992)*

Kidd et al., Phys. Rev. Lett. *88 (2002)*

Li et al. *PRL* **99** 27404 (2007) – “Semimetal to semimetal CDW transition in 1T-$TiSe_2$”

Cu doping of $TiSe_2$





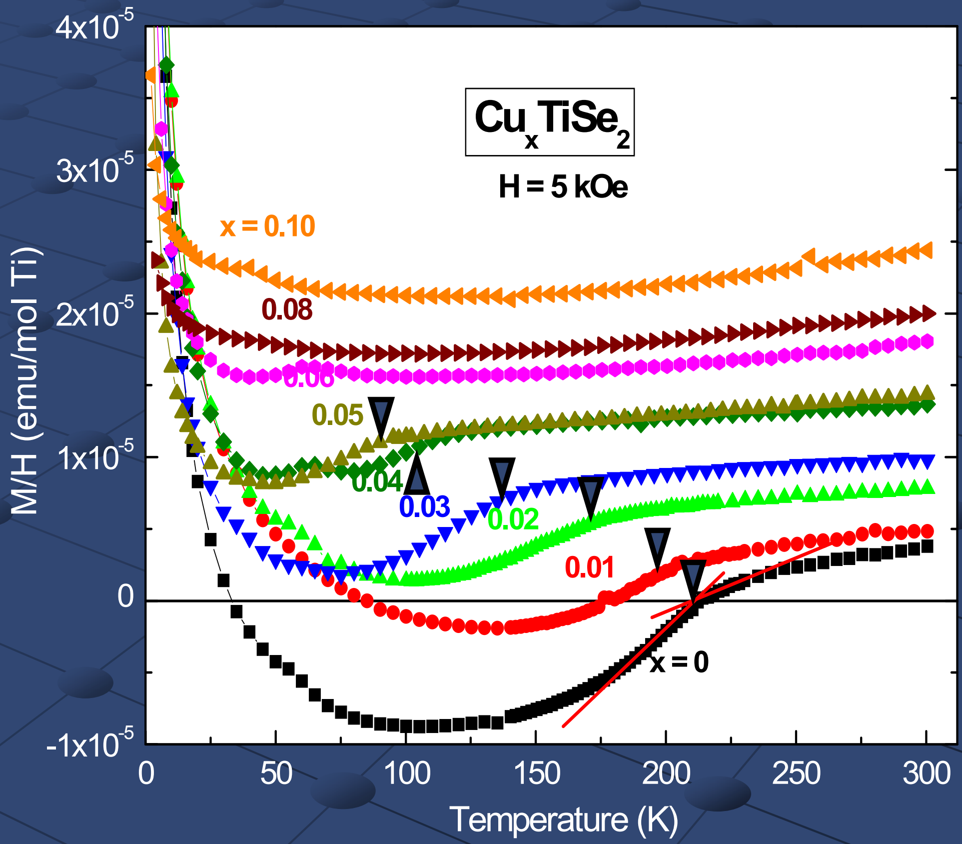
E. Morosan *et al., Nature Physics* **2** (2006)

Cu_xTiSe_2 $(0 \leq x \leq 0.10)$

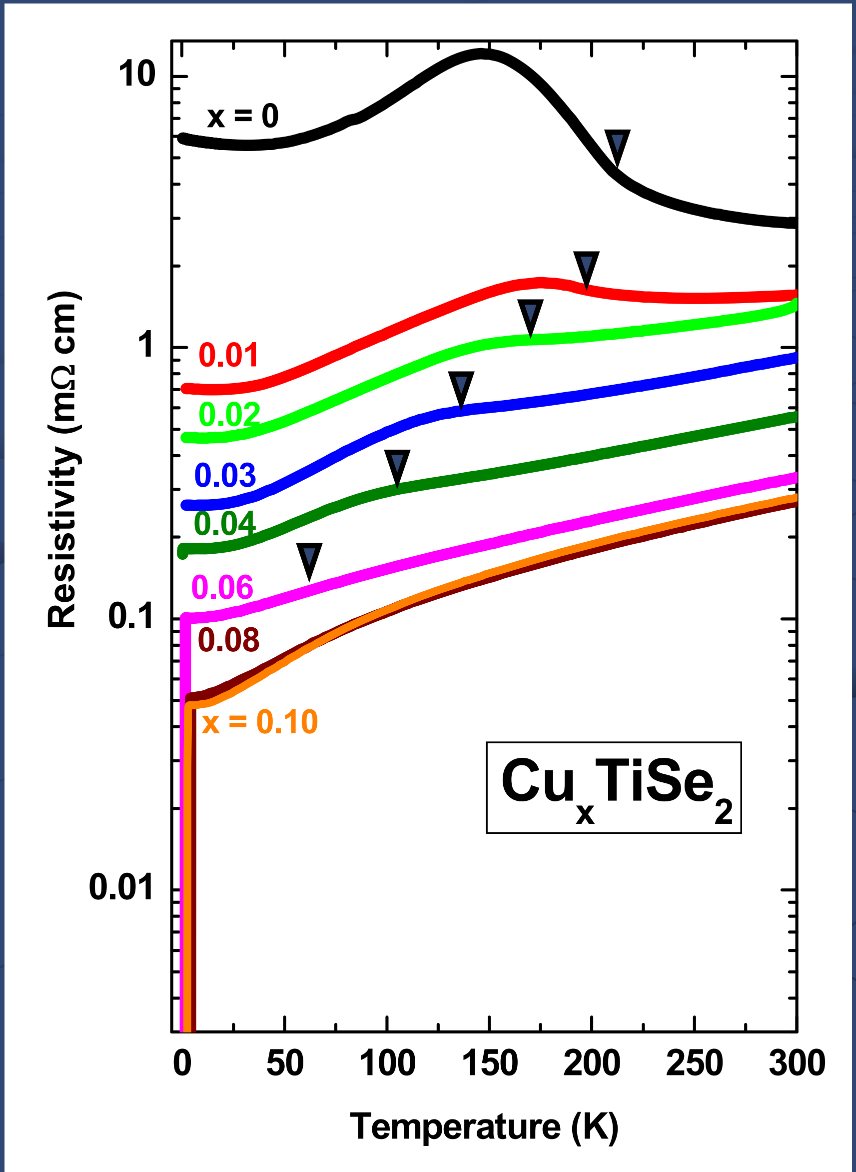
Magnetic susceptibility drops on cooling through CDW transition

As x increases:

- T_{CDW} decreases for $x \leq 0.05$
- $\Delta\chi_{CDW}$ decreases for $x \leq 0.05$
- χ_0 increases

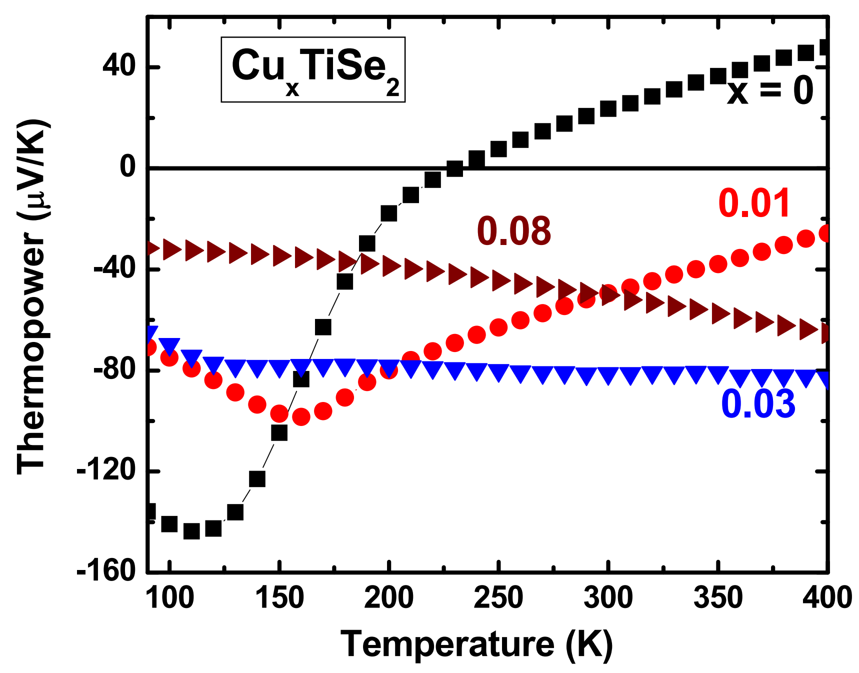


Cu_xTiSe_2 $(0 \leq x \leq 0.10)$



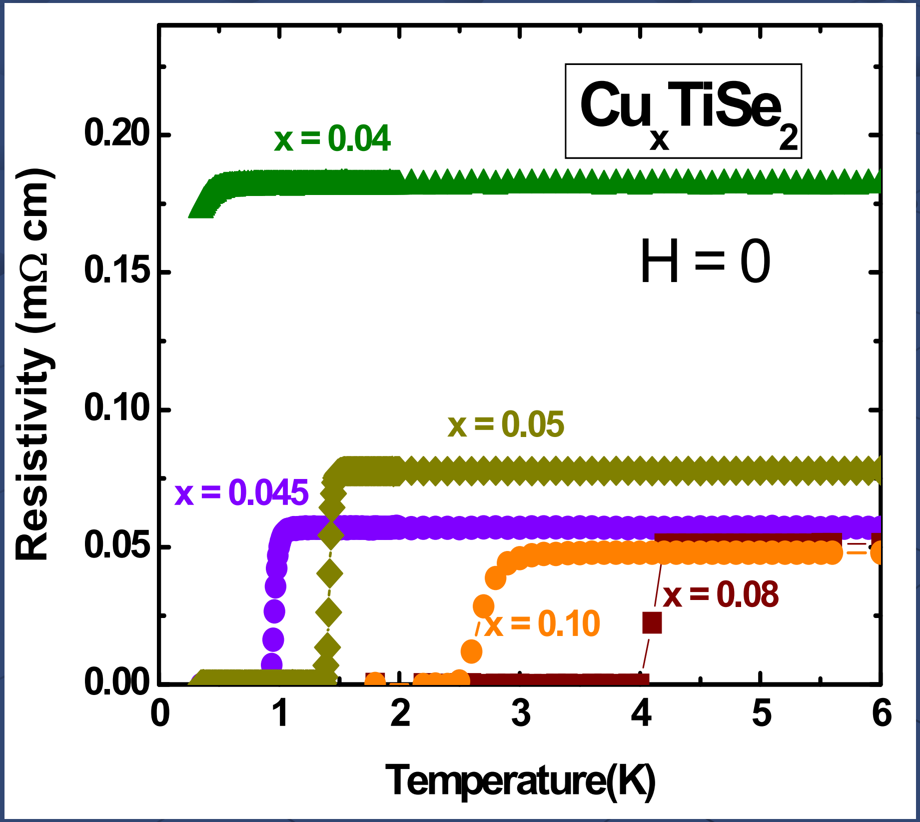
As x increases:

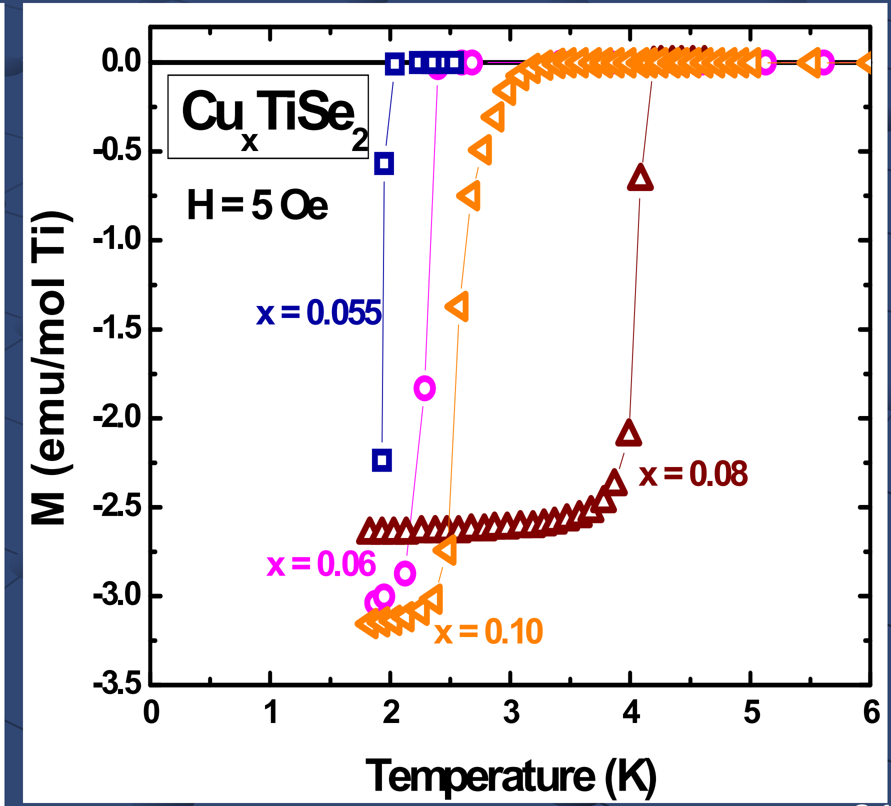
- smaller $\rho(T)$ values – more metallic
- $\rho(300K)/\rho(5K)$ increases
- decreasing $\Delta\rho_{peak}$
- T_{CDW} decreases for $x \leq 0.06$
- superconductivity occurs for $x \geq 0.04$
- $S < 0$ $(x > 0)$: electron doping



The superconducting state in Cu_xTiSe_2

- Superconductivity exists for $0.04 \leq x \leq 0.10$
- T_c maximum for x = 0.08: T_c = 4.15 K





$Cu_{0.08}TiSe_2$ heat capacity

- **Normal state ($T > T_c$):**

$C_p(T) = \gamma T + B\,T^3$

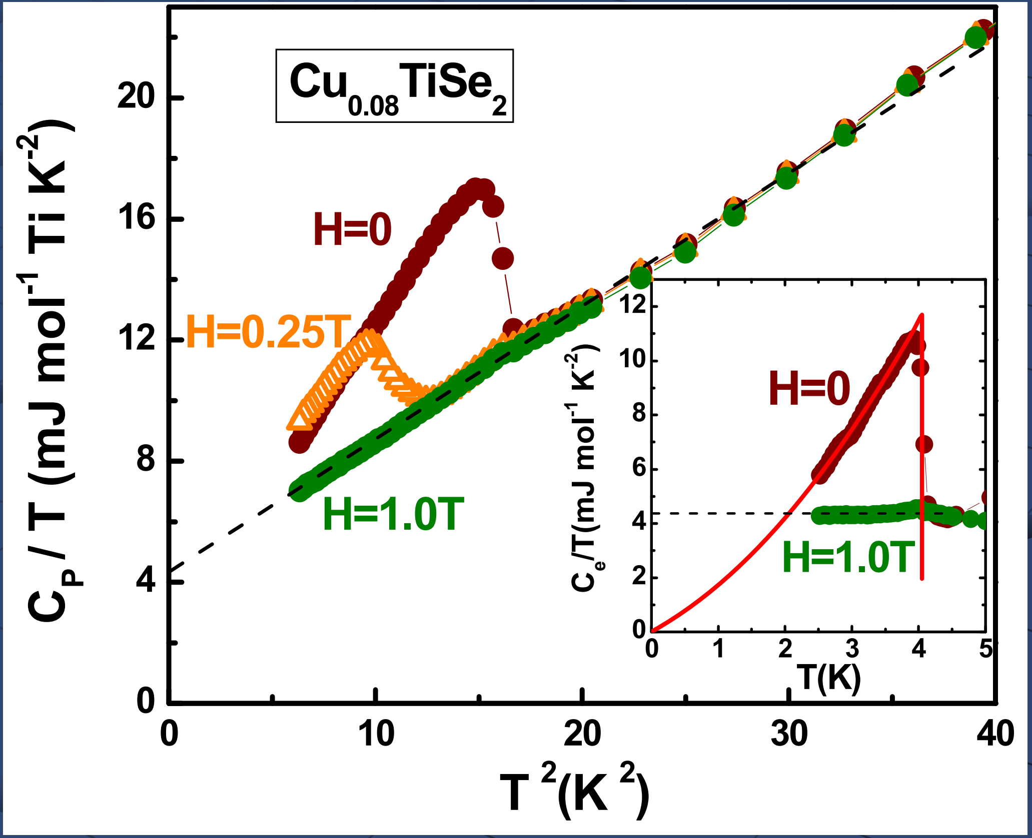
$\gamma = 4.3$ mJ/(mol K^2)

- **The SC phase transition:**

$T_c = 4.15$ K

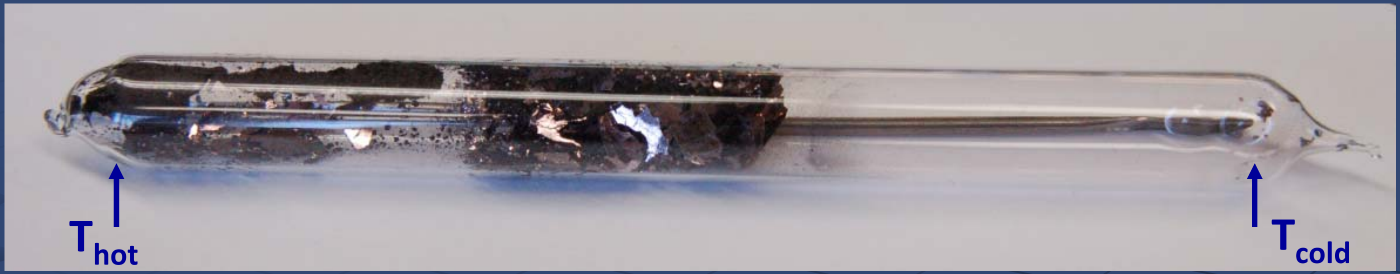
Heat capacity jump:

$\Delta C_e(T_c)/(\gamma T_c) = 1.68$



Cu_xTiSe_2 (single crystals)

$\underline{TiSe_2}$



- Thin hexagonal plates
- Grown via I_2 or excess Se vapor transport

$\underline{Cu_{0.07}TiSe_2}$

apor transport using $CuCl_2$

E. Morosan *et al.*, *Phys. Rev B* **75** (2007) 104505

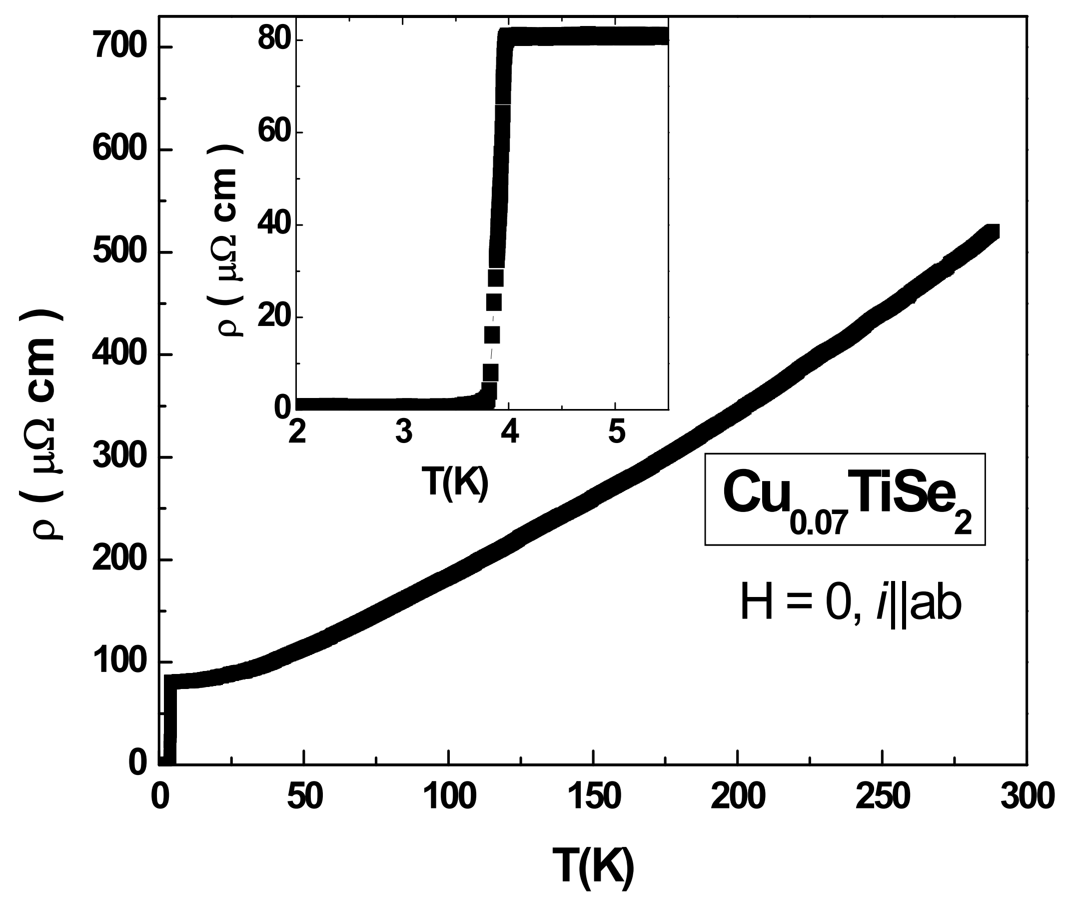
$Cu_{0.07}TiSe_2$ (single crystals) H = 0

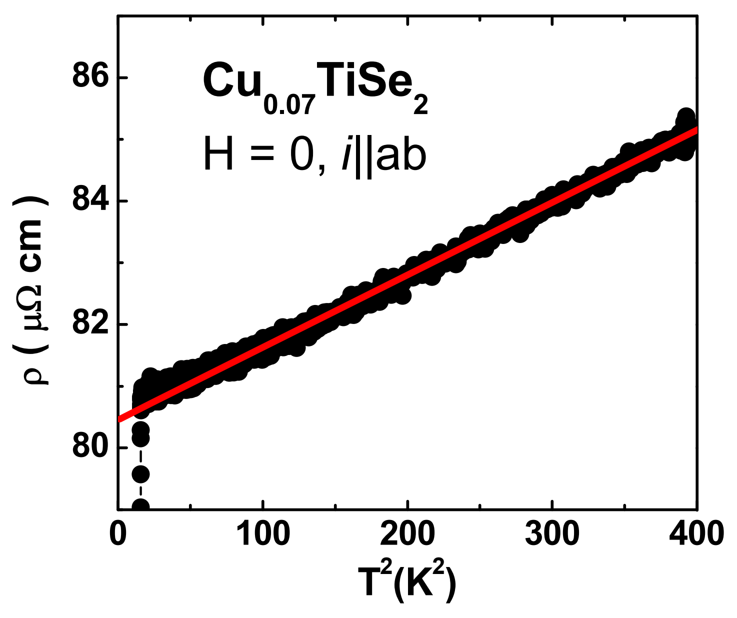
T_c = 3.9 K

RRR = 6.5

High T: $\rho \propto T$

Low T: $\rho \propto T^2$

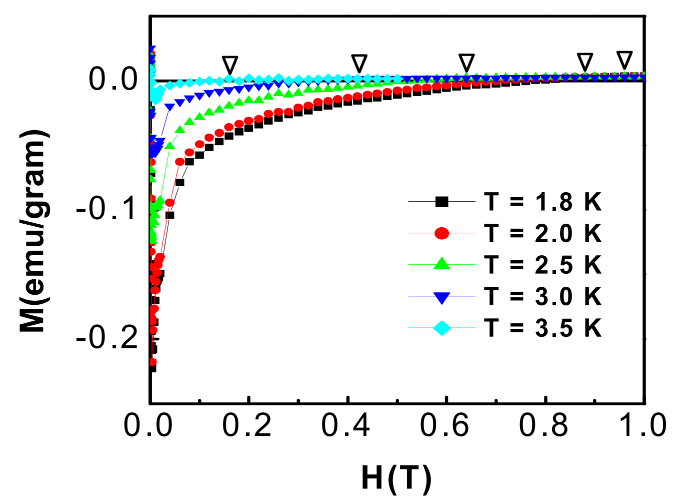




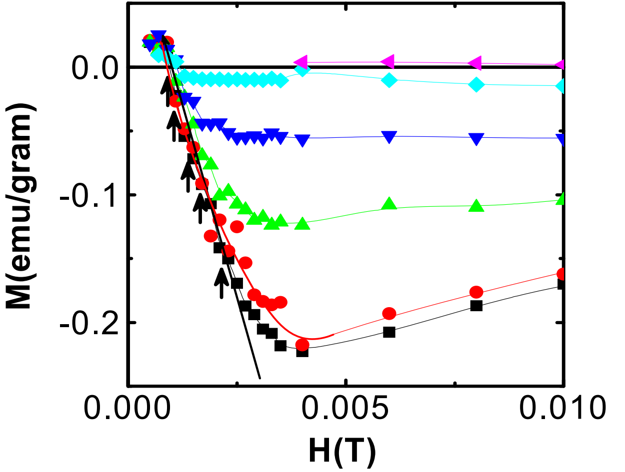
$Cu_{0.07}TiSe_2$ (single crystals): type II superconductor

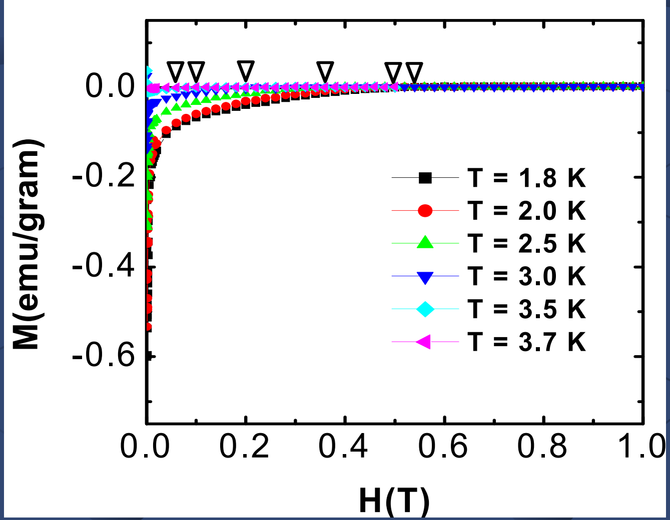
H_{c2}

H_{c1}

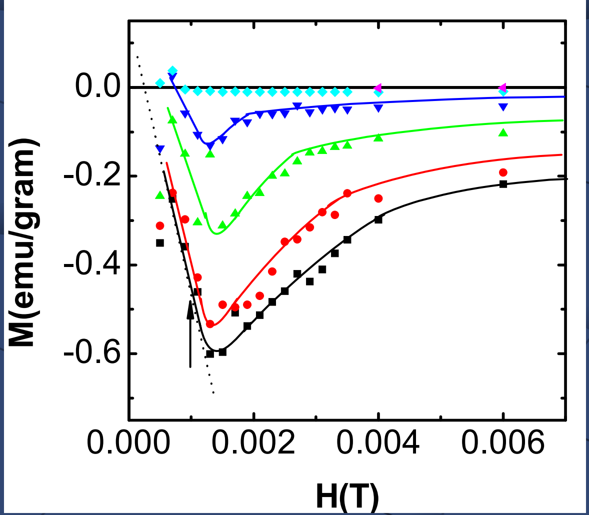


H||ab





H||c



$Cu_{0.07}TiSe_2$ $\rho(H)$

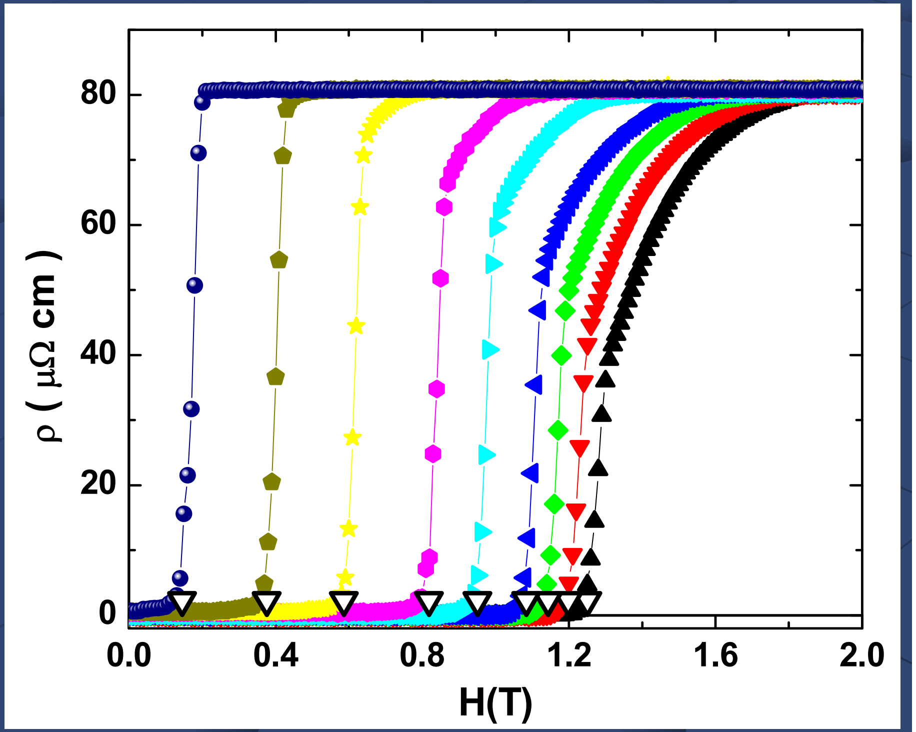
H||ab

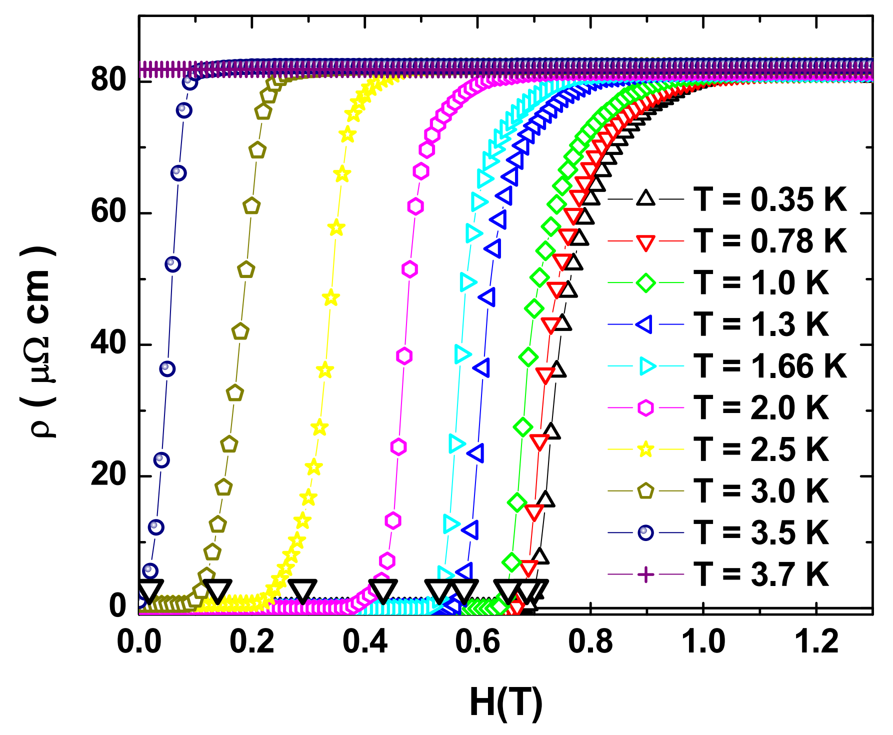
H||c

T = 0.35 K: H_{c2}^{ab} = 1.25 T

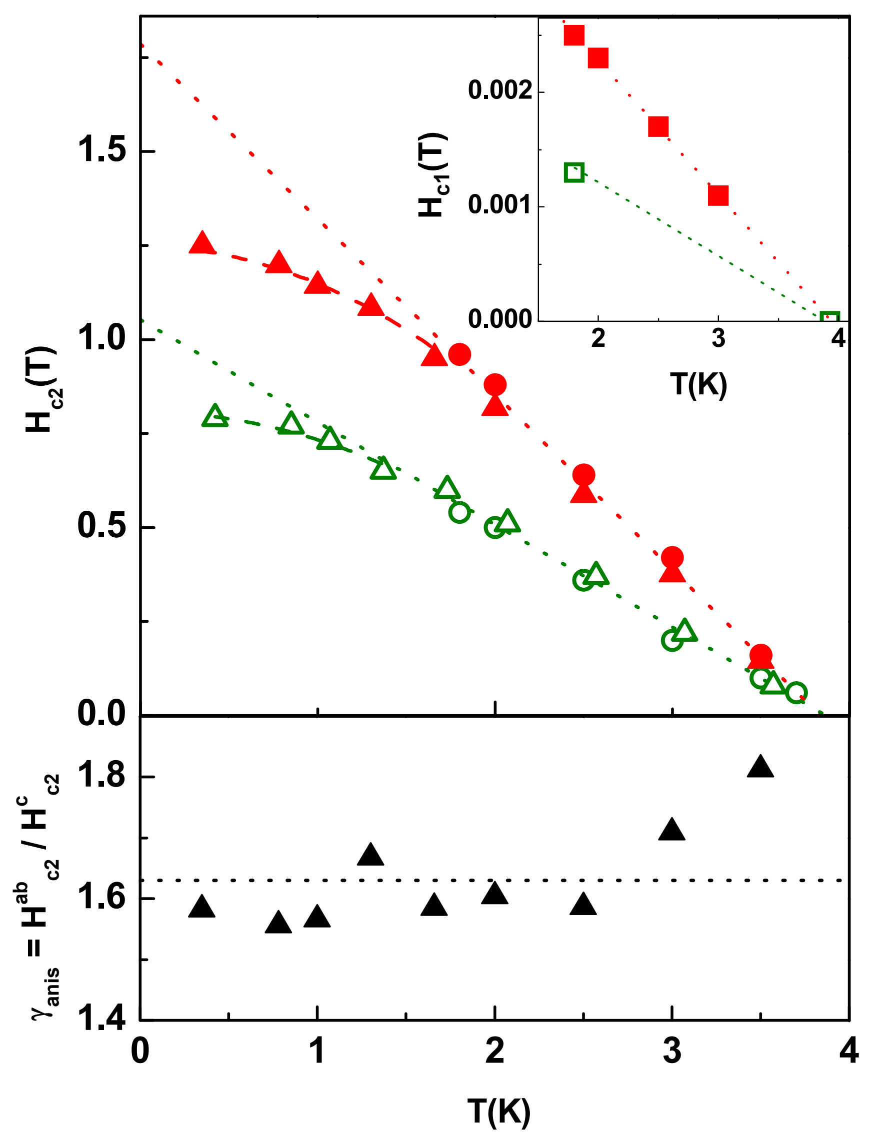
H_{c2}^{c} = 0.7 T

H_{c2}^{ab} and H_{c2}^{c} decrease with T





$Cu_{0.07}TiS_2$ H_c – T phase diagram



T ≈ 0

(Bardeen-Cooper-Schrieffer BCS)

$$H_c(T) \approx H_c(0)\,[1 - 1.07\,(T/T_c)^2]$$

$T \approx T_c$

(Werthamer-Helfand-Hohenberg WHH)

$$H_{c2}(0) \approx 0.693\, H_{c2}{}^*(0)$$

$$H_{c2}{}^*(0) = -\,(dH_{c2}/dT)_{Tc}\,T_c$$

H_{c2} anisotropy: $\gamma_{anis} = H^{ab}{}_{c2}/H^{c}{}_{c2}$

$\gamma_{anis} \approx 1.6$

almost T independent

Anisotropic Ginzburg – Landau theory

$H_{c2}{}^{ab} = \Phi_0 / (2\pi\, \xi_{ab}\, \xi_c)$

$\Rightarrow \xi_{ab}, \xi_c$

$H_{c2}{}^{c} = \Phi_0 / (2\pi\, \xi^2{}_{ab})$

$H_{c2}{}^{i}/H_{c1}{}^{i} = 2\, \kappa_i{}^2/\ln \kappa_i$ $\Rightarrow \kappa_{ab}, \kappa_c$

$\kappa_c = \lambda_{ab}/\xi_{ab}$ $\Rightarrow \lambda_{ab}, \lambda_c$

$\kappa_{ab} = [\lambda_{ab}(0)\, \lambda_c(0)/\xi_{ab}(0)\, \xi_c(0)]^{1/2}$

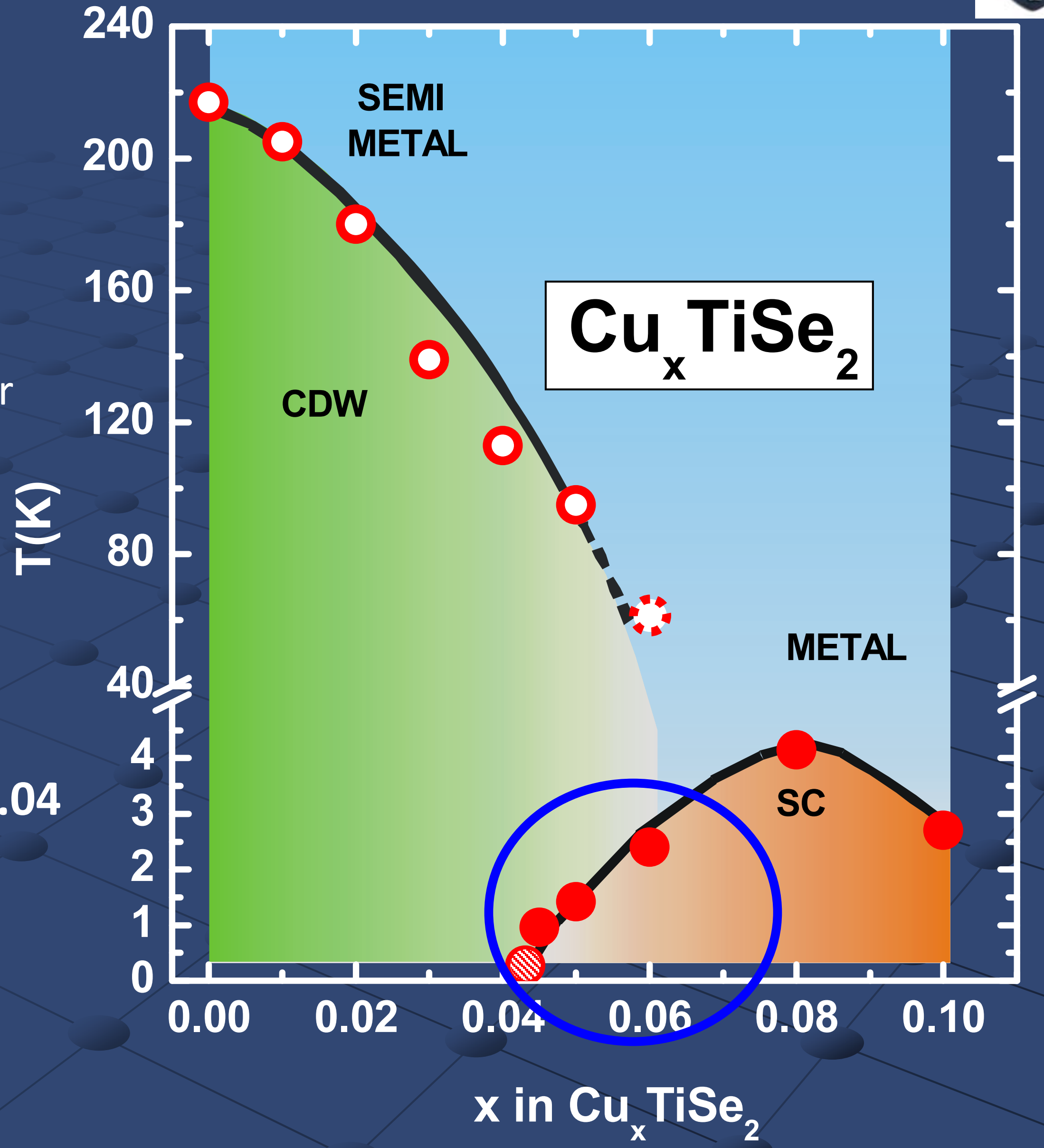
J. R. Clem, *Physica C* **162-164** (1989)

	T_c (K)	ρ_0 ($\mu\Omega$cm)	RRR	$H_{c2}(0)$ (T)	$\xi(0)$ (nm)	$H^*_{c1}(0)$ (Oe)	$\gamma_{anis}(0)$	$\kappa(0)$	$\lambda(0)$ (nm)
H//ab				1.238	21.3	32		25	285
H||c				0.729	12.5	53		13.4	584
	3.9	80	6.5		$\xi_{ab}/\xi_c \approx 1.7$		**1.7**		$\lambda_c/\lambda_{ab} \approx 2$

Cu_xTiSe_2

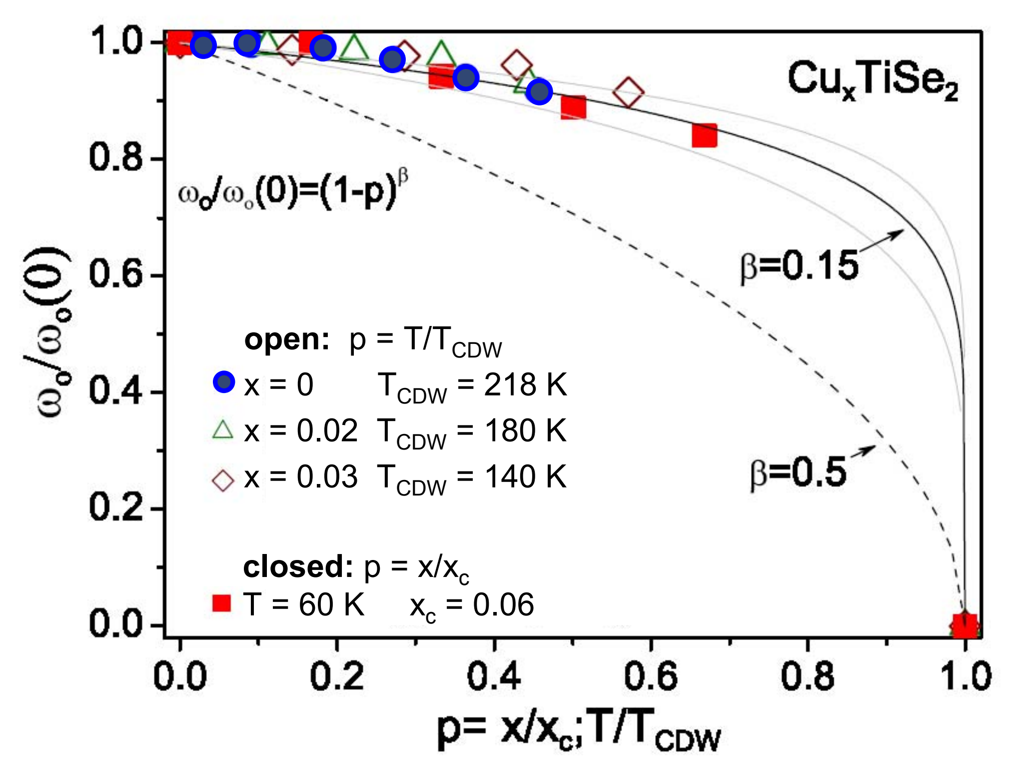
- **How does SC arise?**
  - 2D to 3D transition
  - change in electron count
  - melting of the CDW by disorder

- **What happens below T_c and 0.04 < x < 0.07?**



Cu_xTiSe_2 – Raman spectroscopy

ω_0 - CDW amplitude mode frequency



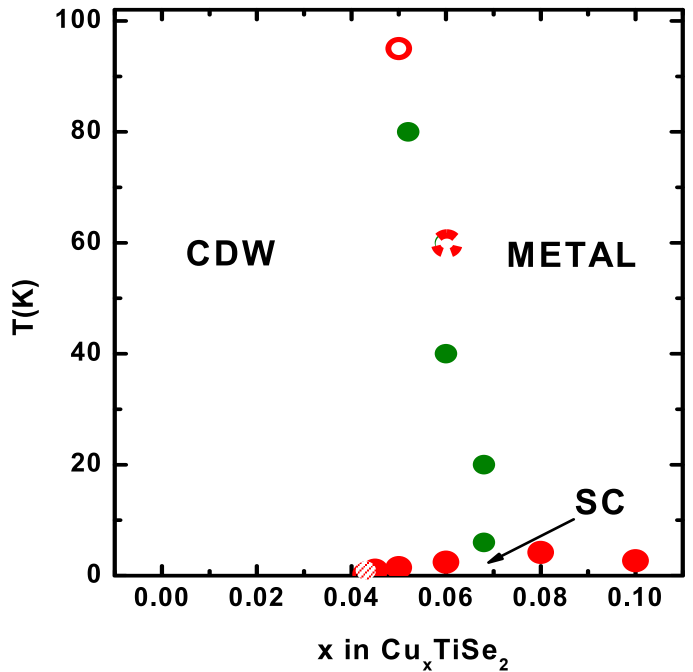
- Identical composition and thermal mode softening

$$\omega_0/\ \omega_0(0) = (1 - p)^\beta$$

$p = x/x_c$ or T/T_{CDW}

$\beta \sim 0.15$

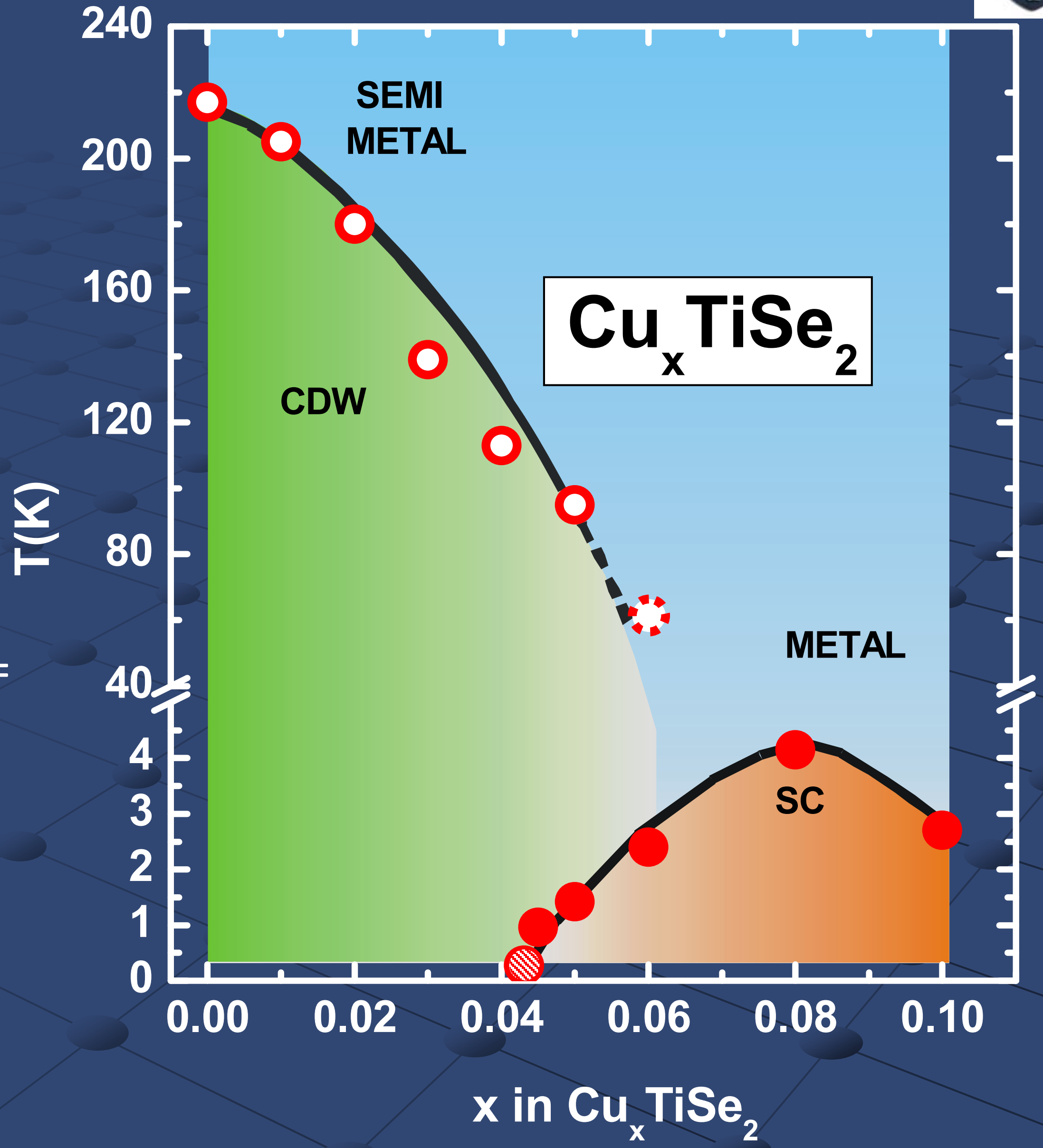
- CDW phase boundary $x_c(T)$ extends below SC dome



H. Barath *et al., PRL* 2008

Cu_xTiSe_2

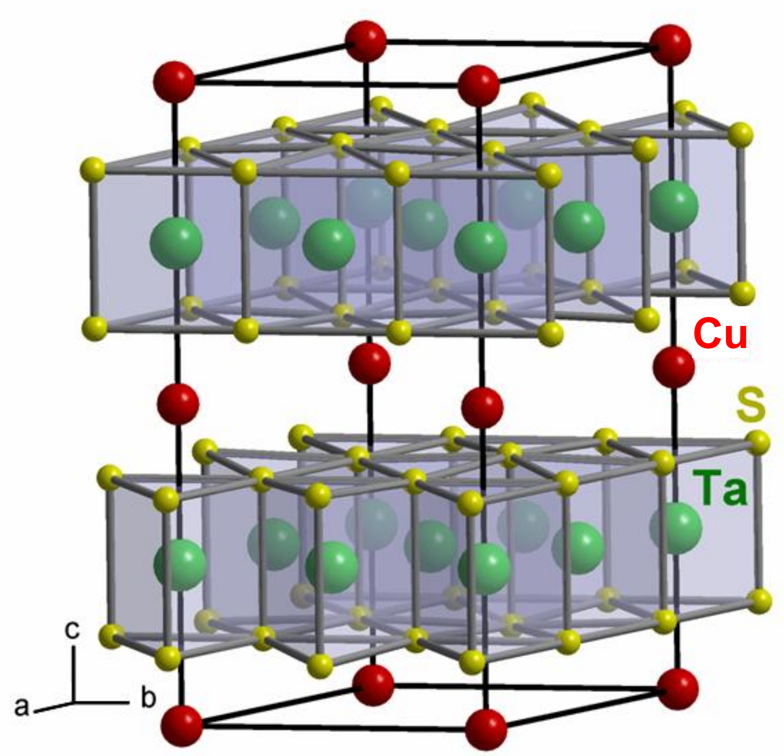
- CDW transition driven down with Cu doping
- SC emerges for $x \geq 0.04$
- CDW and SC coexist for $0.04 < x < 0.06$
- $T_C = 4.15$ K maximum for $x = 0.08$



E. Morosan *et al.*, *Nature Physics* **2** (2006)

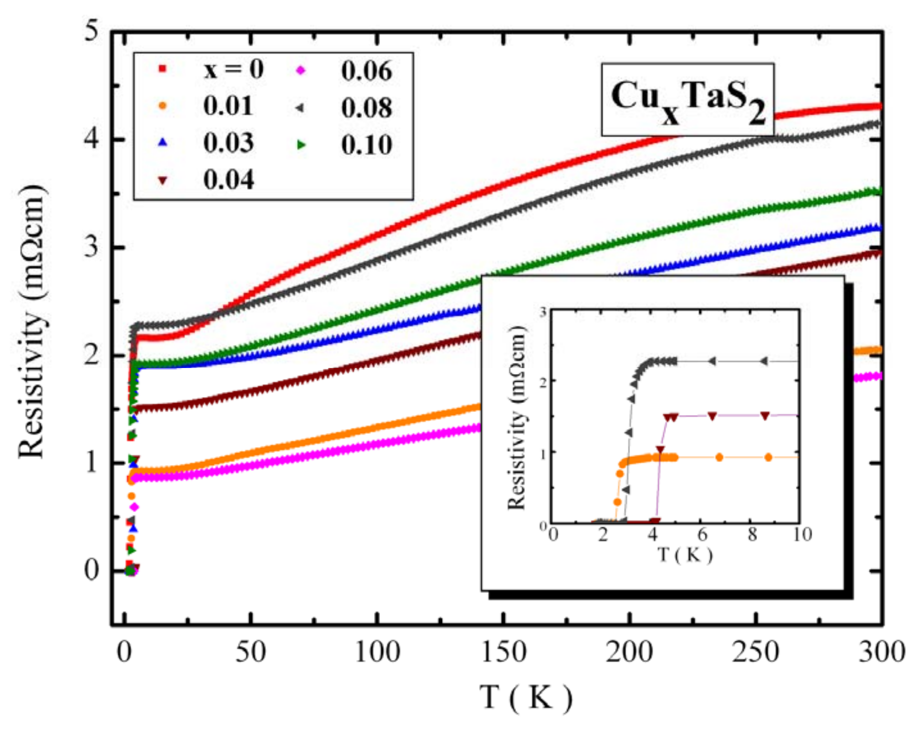
Cu doping of TaS_2

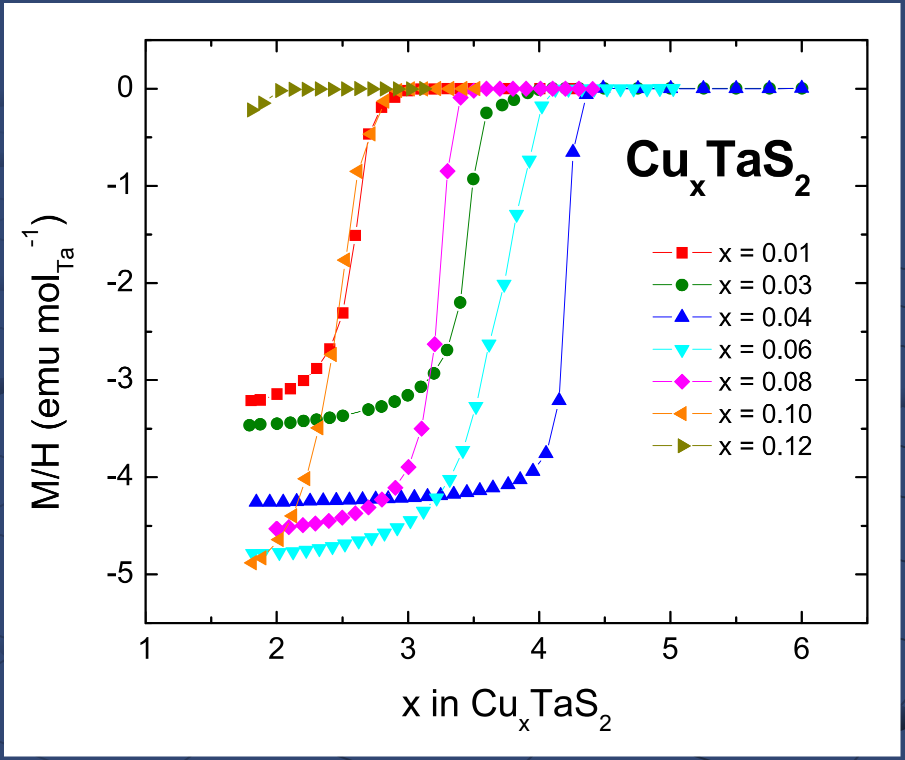
- many known polytypes
- *2H* – TaS_2: superconductivity T_c ~ 0.8 K
- commensurate CDW state below T_{CDW} ~ 75 K
- some differences with Cu_xTiSe_2



K. Wagner *et al.*, *PRB* (2008)

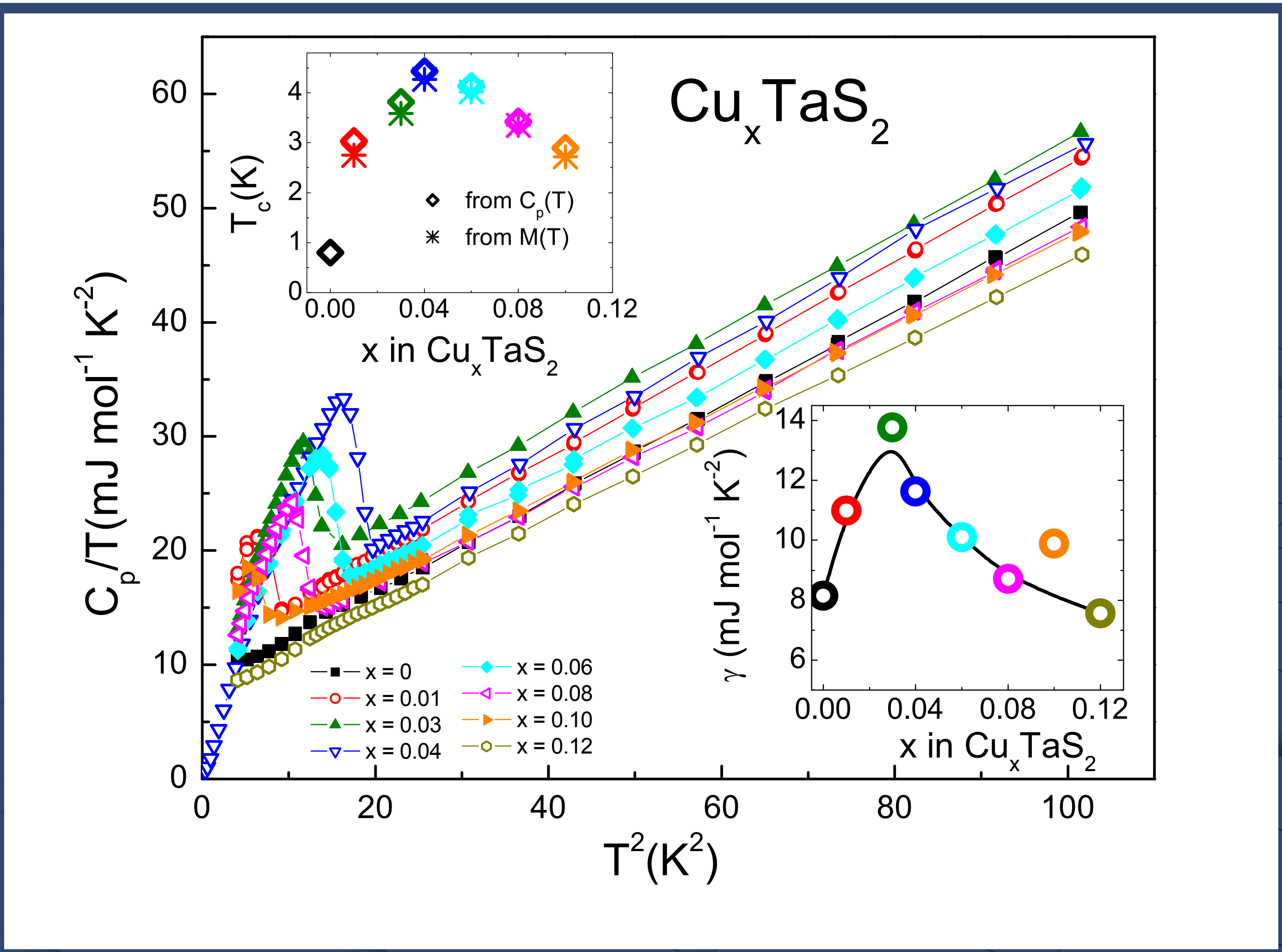
Cu_xTaS_2





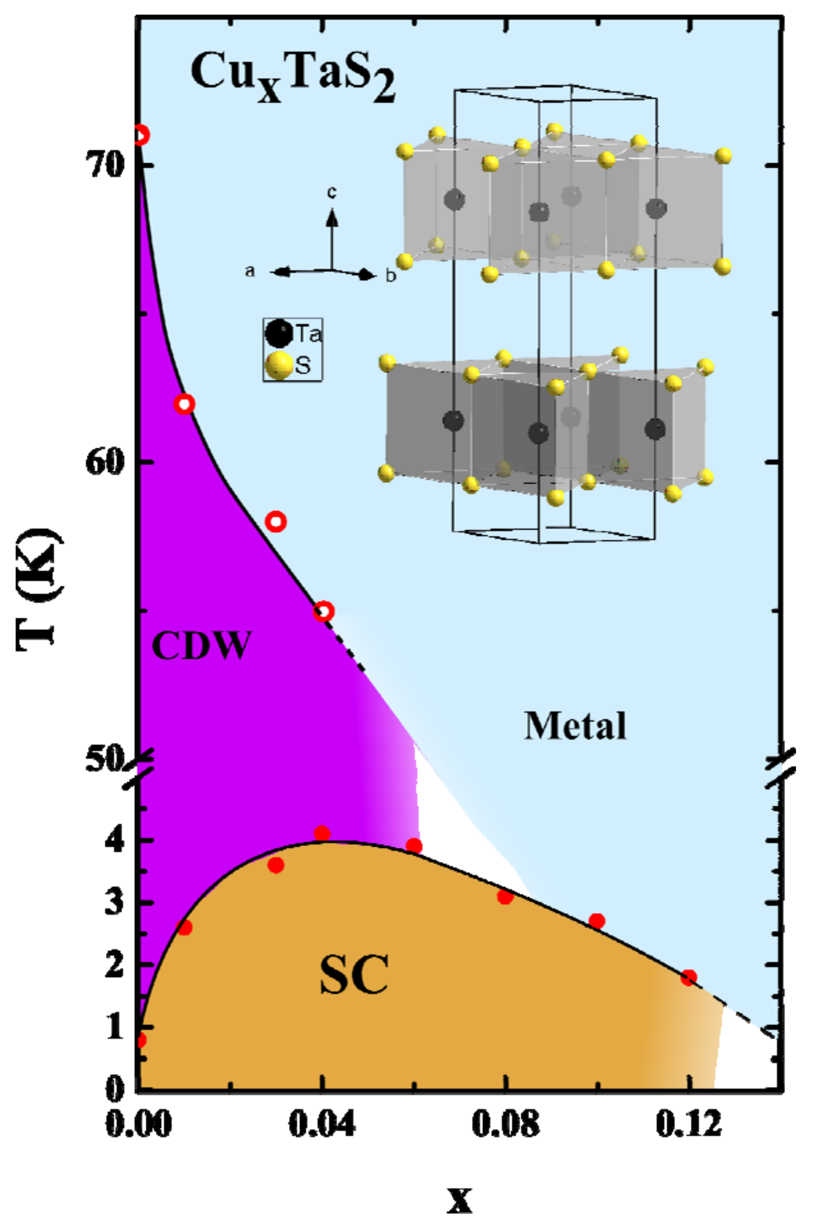
- ρ(T) values decrease with Cu-doping
- non-monotonic x-dependence of T_c
- optimal composition for SC: x ≈ 0.04

K. Wagner *et al.*, *PRB* (2008)



- T_c vs. x – max at x = 0.04
- non-monotonic x-dependence of γ

Cu_xTaS_2



Comparison between Cu_xTiSe_2 and Cu_xTaS_2

1T -$TiSe_2$:

- *commensurate CDW*
  - T_{CDW} = 220 K
  - no FS nesting
- *no superconductivity (SC)*

Cu_xTiSe_2

- *increasing x: monotonous increase in*
  - lattice parameters
  - electronic specific heat coefficient γ
  - M(300K)
- *SC occurs for $x \geq 0.04$*
- *$x_{optimum}$ = 0.08:*
  - T_c = 4.15 K
  - H_{c2} = 1.28 T

2H -TaS_2:

- *more conventional CDW:*
  - incommensurate
  - T_{CDW} = 75 K
  - FS nesting
- *superconductivity: T_c = 0.8 K*

Cu_xTaS_2

- *increasing x:*
  - lattice parameters increase
  - γ = max around $x_{optimum}$ = 0.04
- *T_c almost triples for x = 0.01*
- *$x_{optimum}$ = 0.04:*
  - T_c = 4.45 K
  - H_{c2} = 4.9 T

Conclusions and outlook

- Numerous possibilities to try and design of new, practical superconductors:
  - *use "Fe-As" and blocking B layers to build new crystal structures*
  - *reduce anisotropy by pressure, doping, coupled "Fe-As" layers, "locally layered" structures ($CaFe_4As_3$- type)*
- Doping as tuning parameter between competing ground states in known layered materials
  - *CDW-to-SC induced transition in layered dichalcogenides: Cu_xTiSe_2, Cu_xTaS_2*