Workshop on SCES, ICTP 2015@Trieste, Italy

浙江大學 ZheJiang University

Ambient-pressure superconductivity in Cr_3As_3-chain based materials

Guang-Han Cao
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NSFC

973 CHINA 国家重点基础研究发展计划

Main Collaborators: Jin-Ke Bao, Zhang-Tu Tang, Ji-Yong Liu, Chun-Mu Feng, Zhu-An Xu, and Zeng-Wei Zhu

Outline

- Introduction
- Ambient-pressure SC in $A_2Cr_3As_3$ (A=K,Rb,Cs) (with evidences of unconventional SC)
- Absence of SC in ACr_3As_3 (133)
- Concluding Remarks

J. K. Bao et al., $K_2Cr_3As_3$: PRX 5, 011013 (2015)

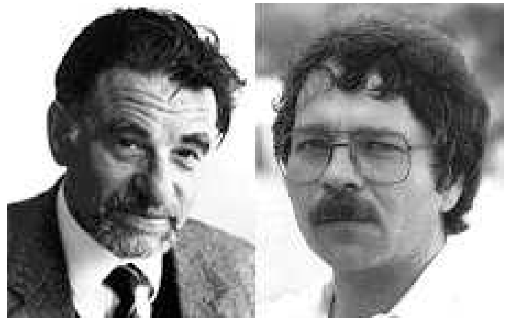
Z. T. Tang et al., $Rb_2Cr_3As_3$: PRB 91, 020506(R) (2015)

Z. T. Tang et al., $Cs_2Cr_3As_3$: Sci. China Mater. 58, 16 (2015)

J. K. Bao et al., KCr_3As_3: PRB 91, 180404(R) (2015)

Z. T, Tang et al., $RbCr_3As_3$ and $CsCr_3As_3$: Sci. China Mater. 58, 543 (2015)

New SCs: either higher Tc or Exotic SC



Room-temperature Superconductors

1911 — 1986 — 20??

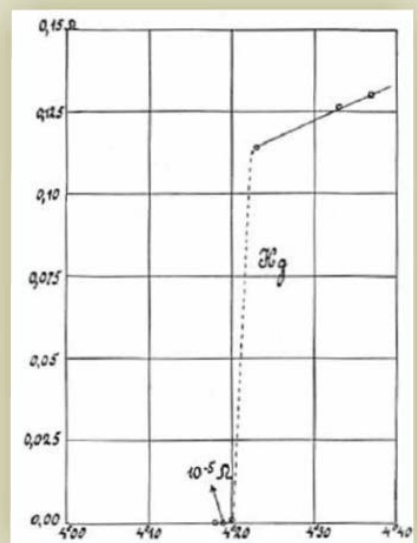


Figure 4. Historic plot of resistance (ohms) versus temperature (kelvin) for mercury from the 26 October 1911 experiment shows the superconducting transition at 4.20 K. Within 0.01 K, the resistance jumps from unmeasurably small (less than 10^{-5} Ω) to 0.1 Ω (from ref. 4.)

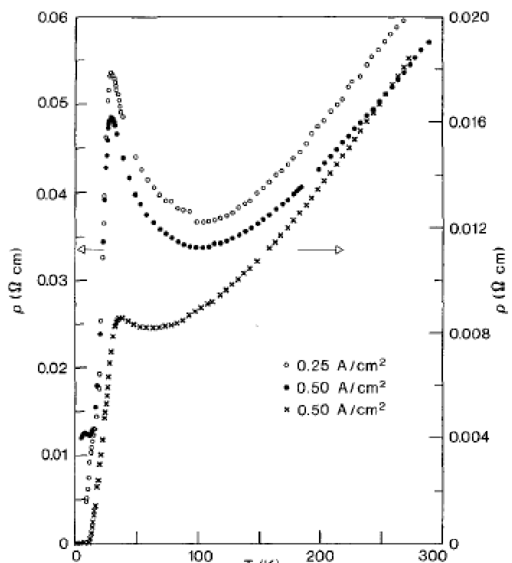


Fig. 1. Temperature dependence of resistivity in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ for samples with $x(Ba)=1$ (upper curves, left scale) and $x(Ba)=0.75$ (lower curve, right scale). The first two cases also show the influence of current density

One of Holy Grails in physical sciences

Conventional — Unconventional — Mechanism of USC

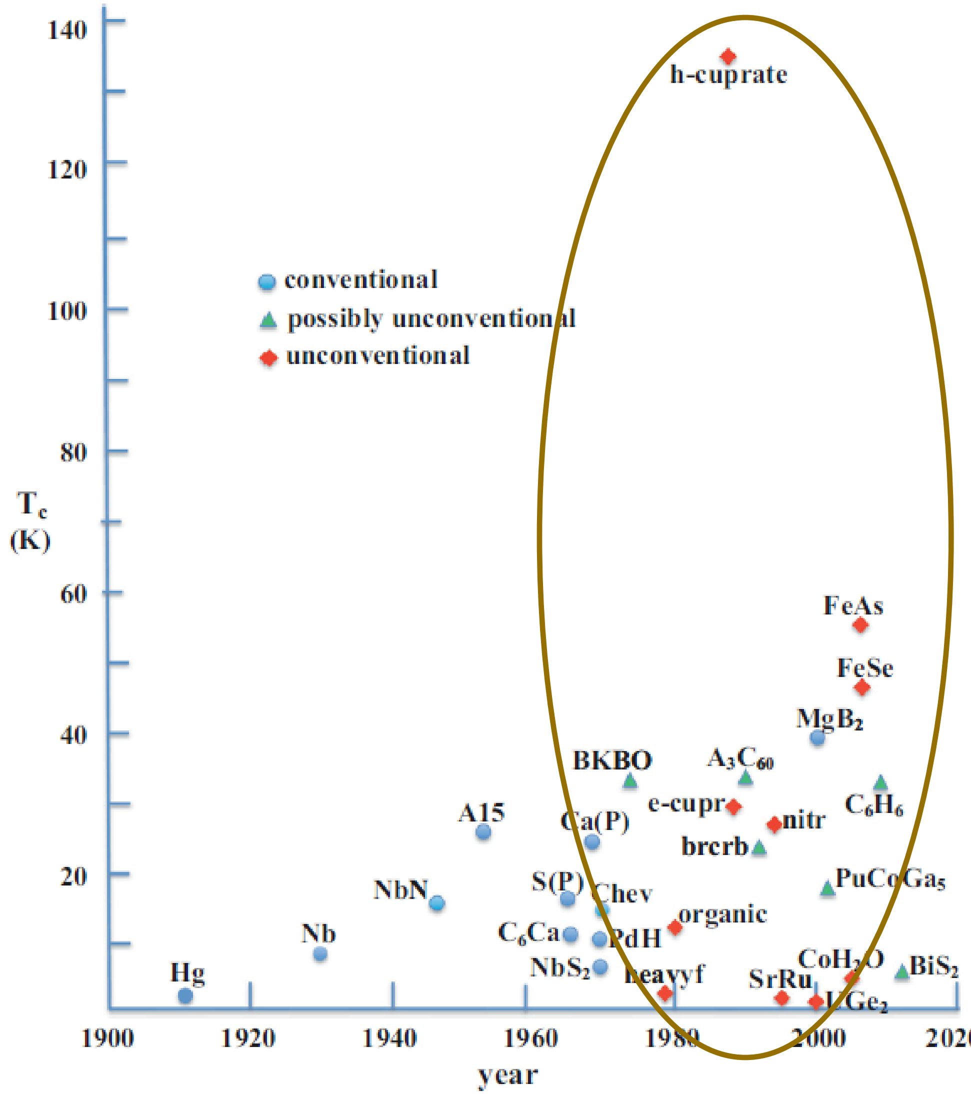
32 class of SCs categorized in terms of “conventionality”

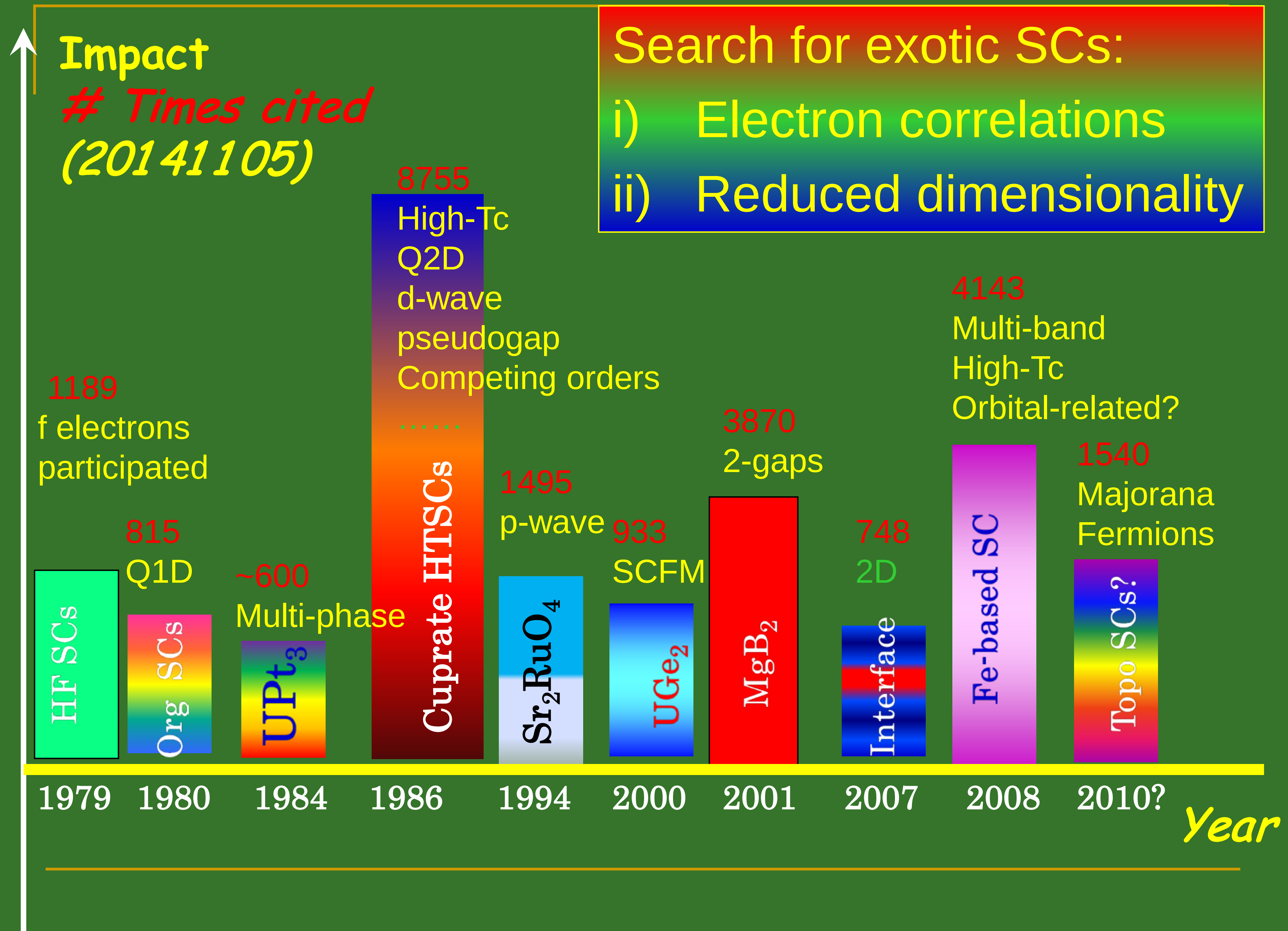
Editorial Physica C 514 (2015) 1–8

Hirsch, Maple & Marsiglio

Superconducting materials classes: Introduction and overview

	Material class	Year	Max T_c m	Category
C1	Elements,	1911	Nb	conv
	alloys and simple compounds	1912	NbN	conv
C2	A15's	1954	Nb_3Ge	conv
C3	Doped semiconductors	1964	CB_x	conv
C4	Insul. elements under pressure	1964	S	conv
C5	Intercalated graphite	1965	C_6Ca	conv
C6	Metallic elements under pressure	1968	Ca	conv
C7	Hydrogen-rich materials	1970	PdD	conv
C8	Layered t. m. dichalcogenides	1970	NbS_2	conv.
C9	Chevrel phases	1971	$PbMo_6S_8$	conv
C10	Magnetic superconductors	1972	$ErRh_4B_4$	conv
C11	Thin films	1978		conv
C12	Magnesium diboride	2001	MgB_2	conv
P1	Bismuthates	1975	$Ba_{1-x}K_xBi$	poss unc
P2	Fullerenes	1991	$RbCs_2C_{60}$	poss unc
P3	Borocarbides	1993	$YPd_5B_3C_{0.}$	poss unc
P4	Plutonium compounds	2002	$PuCoGa_5$	poss unc
P5	Interface superconductivity	2007	$LaAlO_3/Sr$	poss unc
P6	Aromatic hydrocarbons	2010	K-doped I	poss unc
P7	Doped top. ins.	2010	$Cu_x(PbSe)$	poss unc
P8	BiS_2-based materials	2012	$YbO_{0.5}F_{0.5}$	poss unc
P9	Unstable/elusive sc	1946	C–S	poss unc
U1	Heavy fermions	1979	UPd_2Al_3	unconv
U2	Organic charge-transfer	1980	(BEDT-TT	unconv
U3	Cuprates hole-doped	1986	$HgBa_2Ca_2$	unconv
U4	Cuprates e-doped	1989	$Sr_{0.9}La_xCu$	unconv
U5	Strontium ruthenate	1994	Sr_2RuO_4	unconv
U6	Layered nitrides	1996	Ca(THF)H	unconv
U7	Ferromagnetic sc	2000	UGe_2	unconv
U8	Cobalt oxyde hydrate	2003	$Na_x(H_3O)_z$	unconv
U9	Non-centro-symmetric	2004	$SrPtSi_3$	unconv
U10	Iron pnictides	2008	$SmFeAsO$	unconv
U11	Iron chalcogenides	2008	$Na_xFe_2Se_2$	unconv





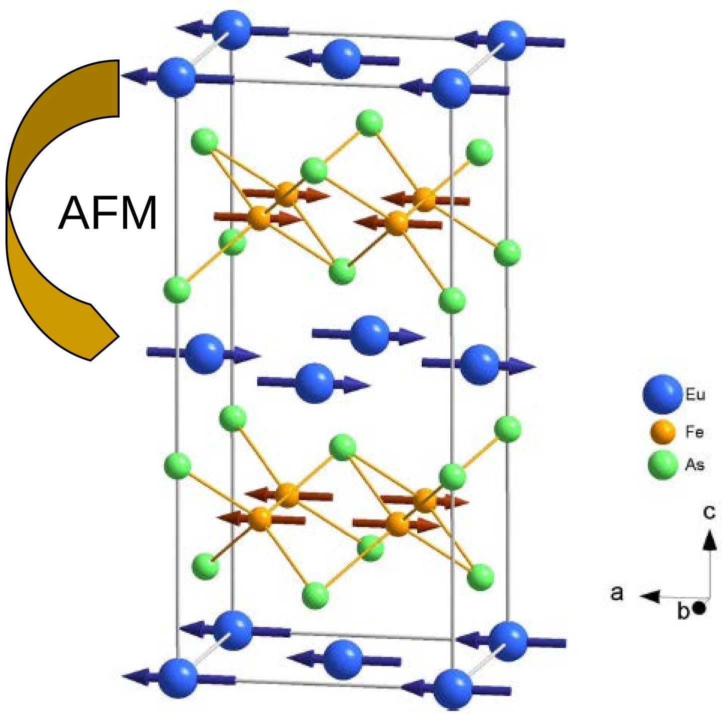
Impact
Times cited
(20141105)
Search for exotic SCs:
i) Electron correlations
ii) Reduced dimensionality
1189
f electrons
participated
HF SCs
815
Q1D
Org SCs
~600
Multi-phase
UPt3
8755
High-Tc
Q2D
d-wave
pseudogap
Competing orders
……
Cuprate HTSCs
1495
p-wave
Sr2RuO4
933
SCFM
UGe2
3870
2-gaps
MgB2
748
2D
Interface
4143
Multi-band
High-Tc
Orbital-related?
Fe-based SC
1540
Majorana
Fermions
Topo SCs?
1979
1980
1984
1986
1994
2000
2001
2007
2008
2010?
Year

A Brief Introduction to New Superconductors recently discovered in Our Group

$EuFe_2As_2$:

striped Fe3d AFM

A-type Eu4f AFM

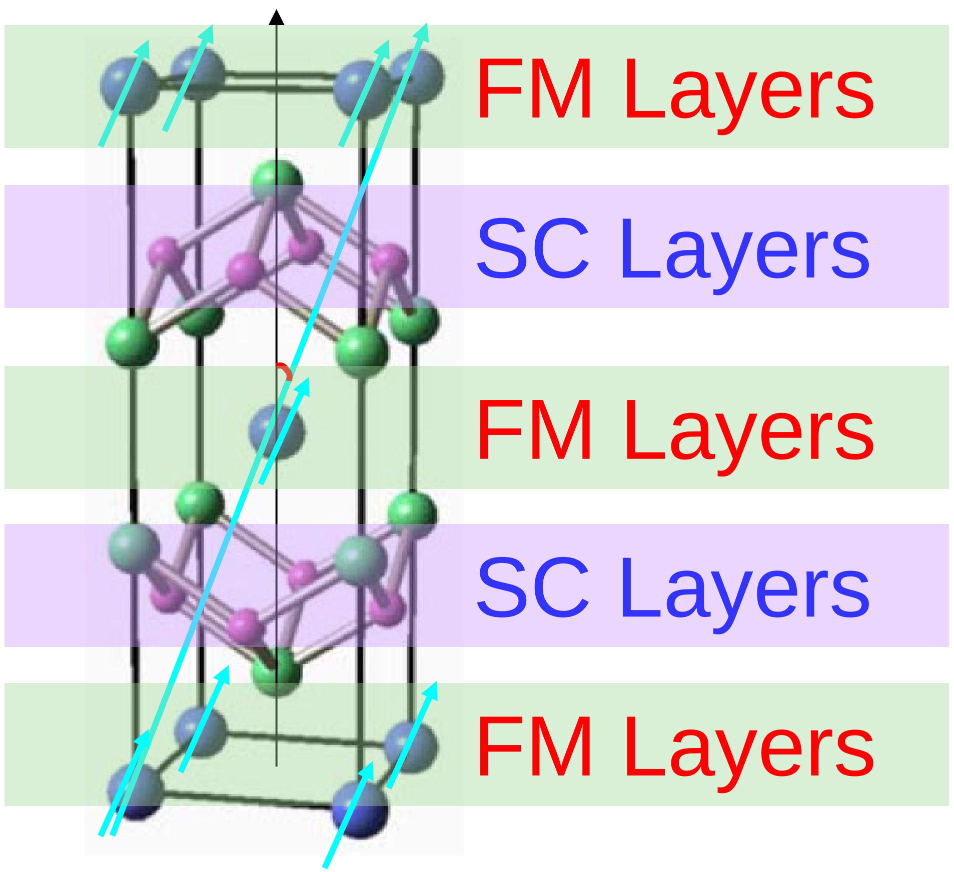


Y. Yao et al., PRB **80**, 174424 (2009)

$EuFe_2(As,P)_2$:

FM Eu4f; SC Fe3d

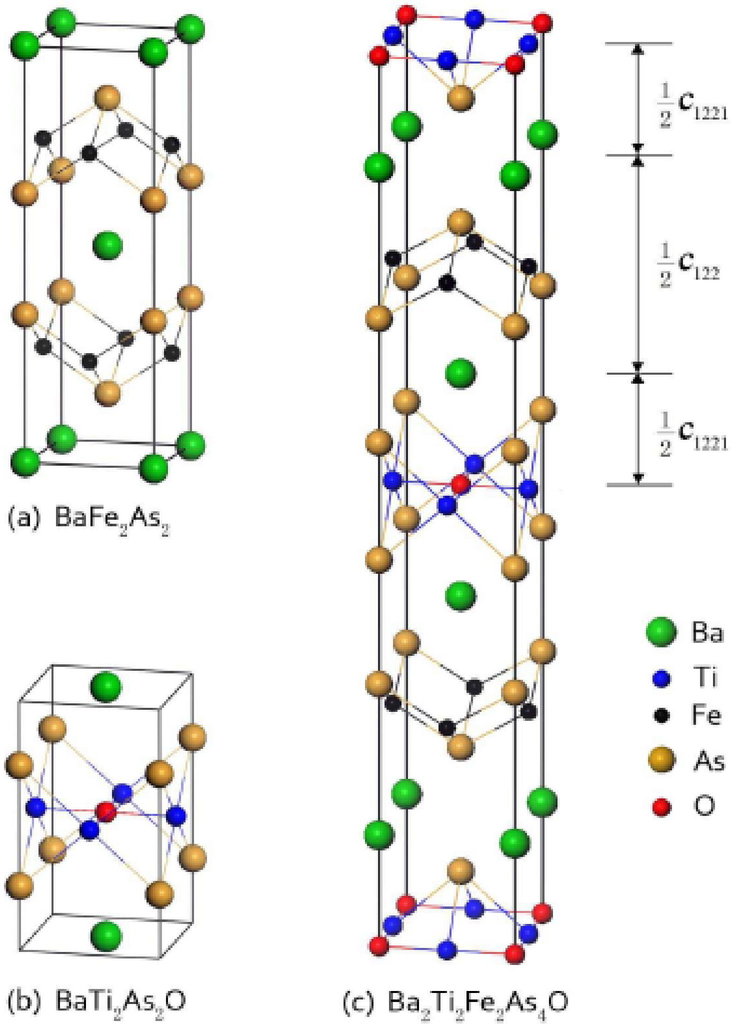
Z. Ren et al., PRL102, 137002 (2009)

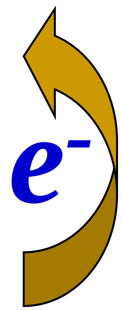


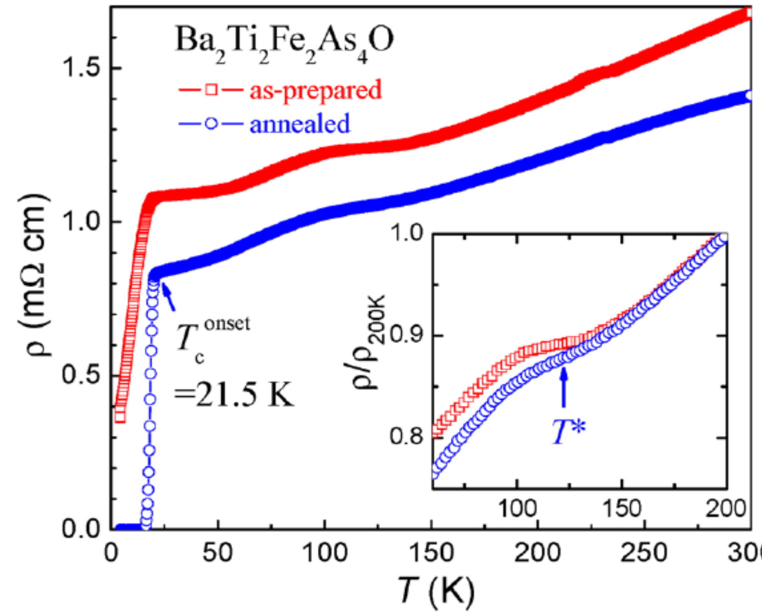
Eu spins are basically along c-axis with a possibly small canting

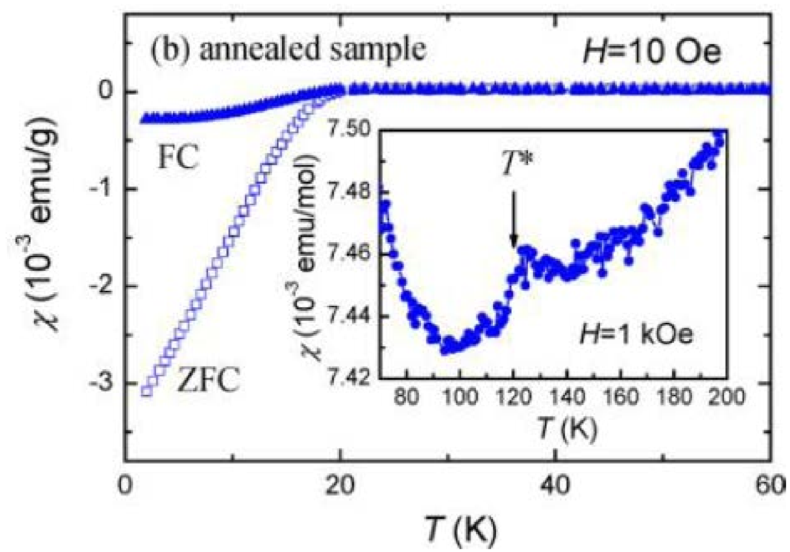
Self-doped SC

$Ba_2Ti_2Fe_2As_4O$ (22241)







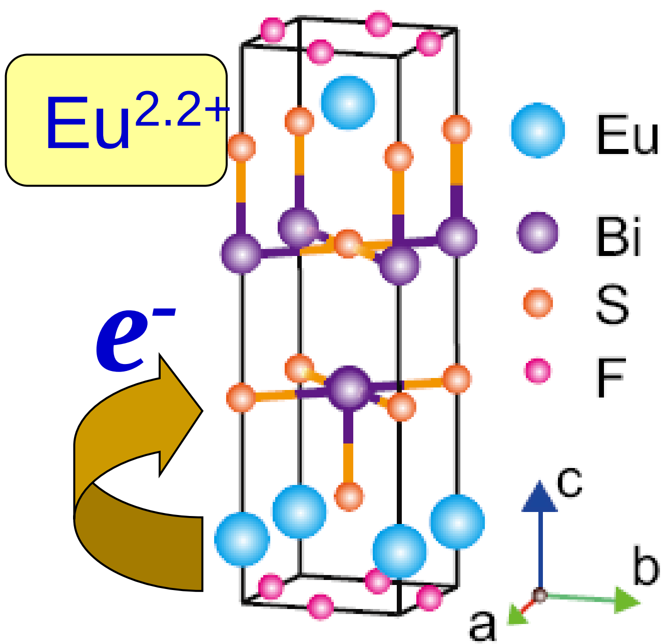


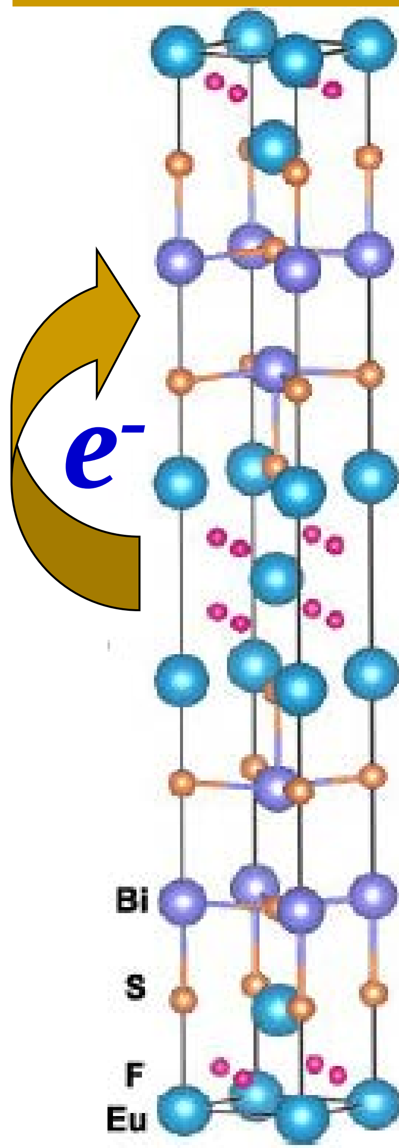
Y. L. Sun et al., JACS 134, 12893 (2012)

Zhai et al., JACS 136, 15386 (2014)

Compounds with BiS_2 bilayers: doped band insulator→SC

→New BiS_2-bilayer based SCs Via self doping





Eu-BVS
χ(T)
Mossbauer

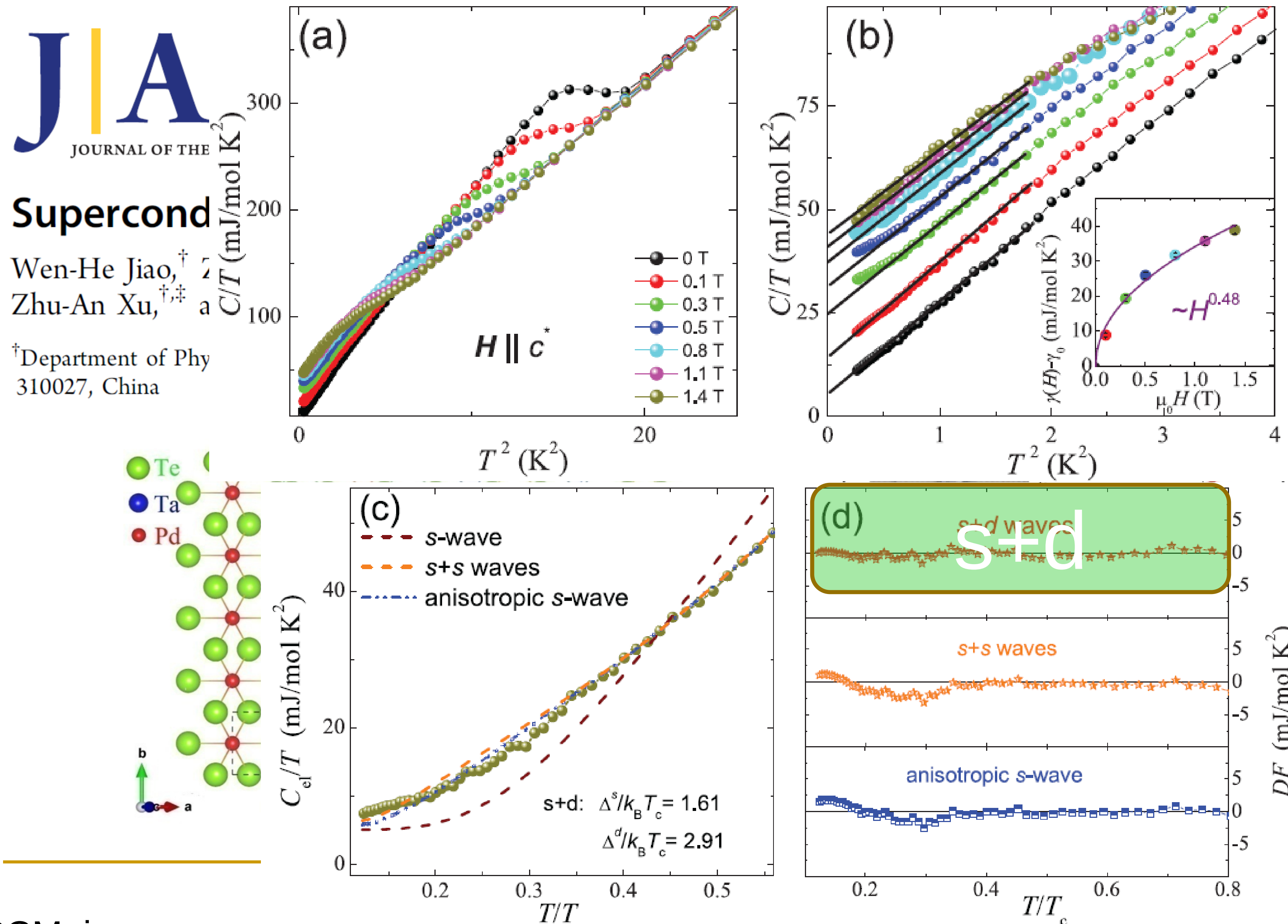
→Eu^{2+}
→$Eu^{2.6+}$
→Eu^{2+}

Self doping of x=0.3

H. F. Zhai et al., PRB 90, 064518 (2014)

Self-doped SC

Superconductivity at 4.6 K in $Ta_4Pd_3Te_{16}$



JoPCM, in press

Summary of the new SCs in our Group

- 2009-2013

  FMSC in iron pnictides: Eu122 system

- 2012-2014 Design and self doping:

  $Ba_2Ti_2Fe_2As_4O$, $EuBiS_2F$ and $Eu_3Bi_2S_4F_4$

- 2014 low-dimensional telluride: $Ta_4Pd_3Te_{16}$

- 2014-2015 New quasi-1D Compounds:

  $A_2Cr_3As_3$

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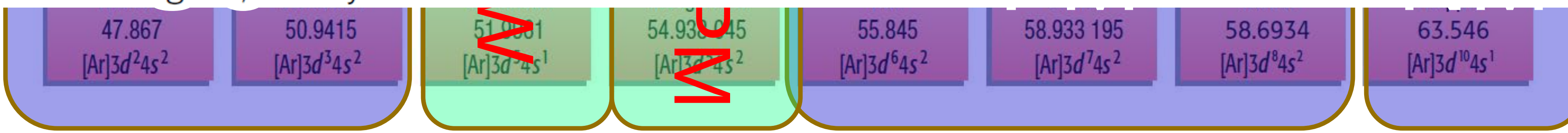
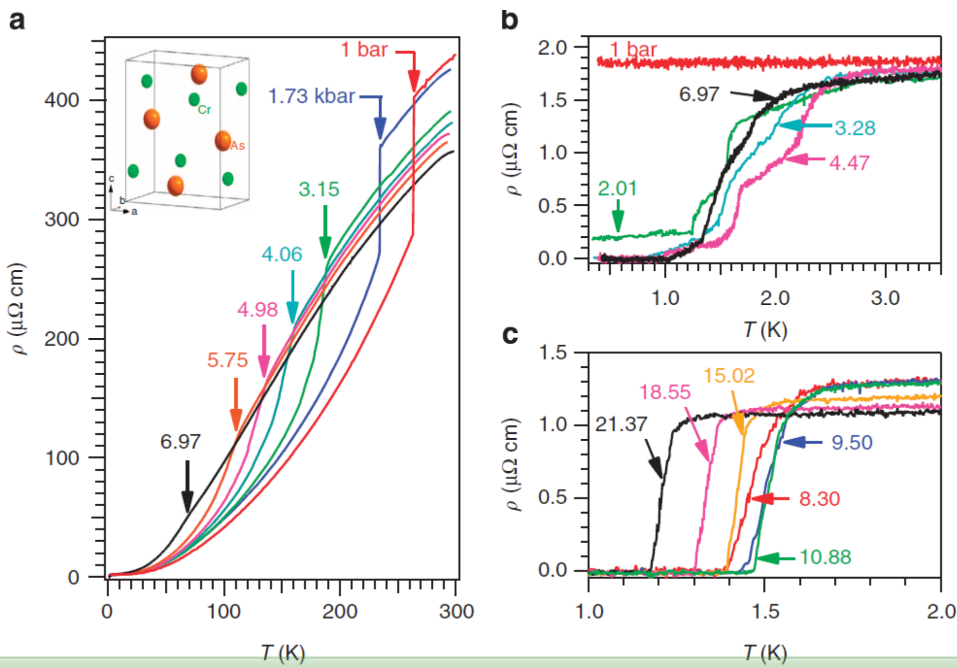
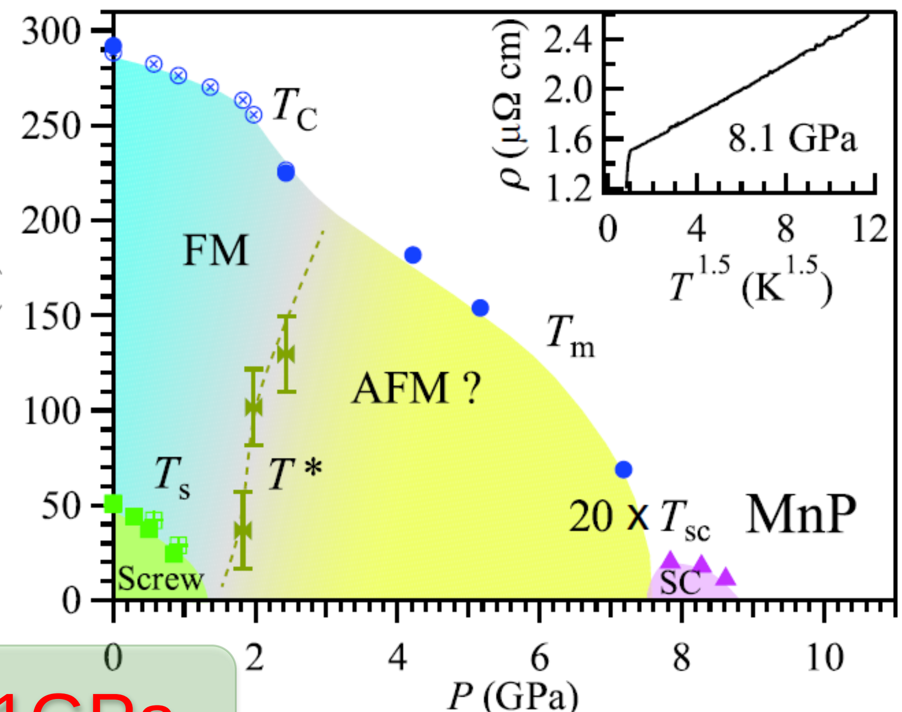
DOI: 10.1038/ncomms6508

Superconductivity in the vicinity of antiferromagnetic order in CrAs

Wei Wu[1,*], Jinguang Cheng[1,2,*], Kazuyuki Matsubayashi[2], Panpan Kong[1], Fukun Lin[1], Changqing Jin[1,3], Nanlin Wang[1,3,4], Yoshiya Uwatoko[2] & Jianlin Luo[1,3]







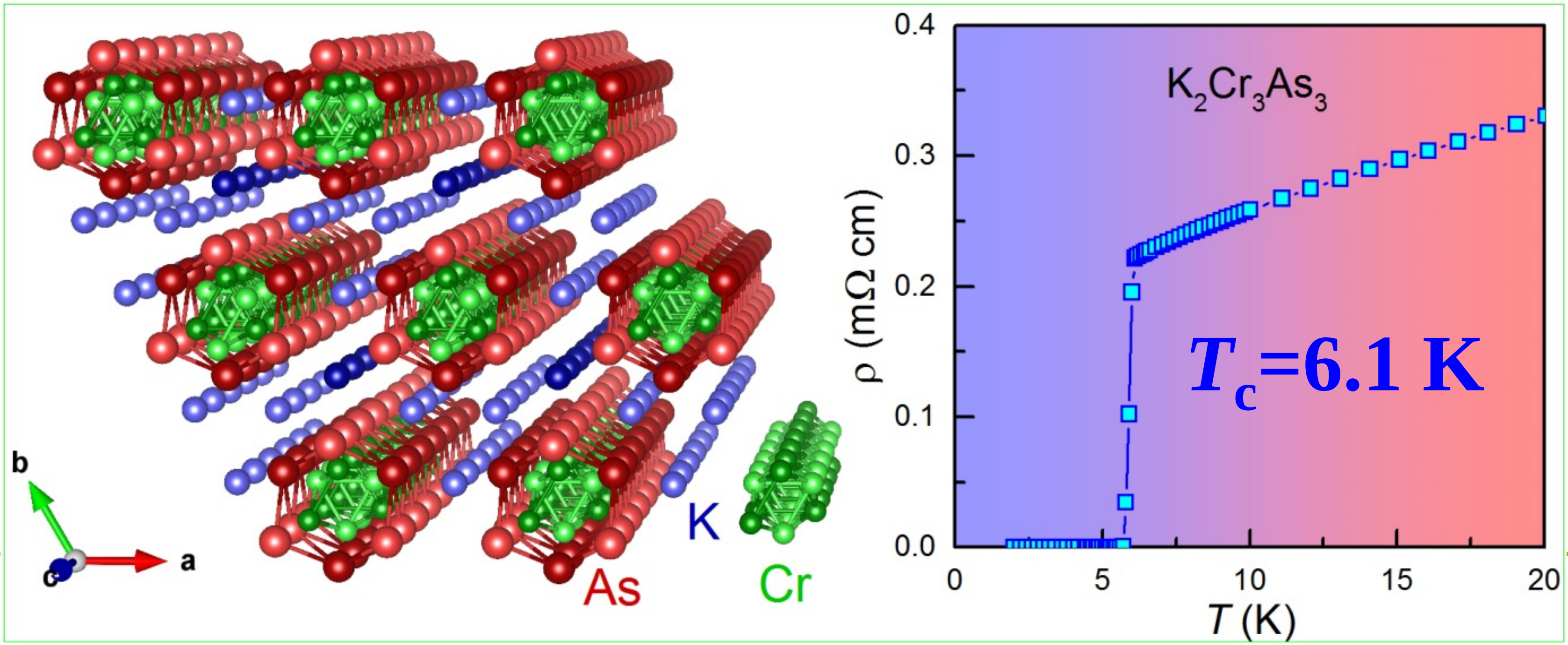
SC at ~2 K in CrAs under ~ 1GPa

PHYSICAL REVIEW X 5, 011013 (2015)

Superconductivity in Quasi-One-Dimensional $K_2Cr_3As_3$ with Significant Electron Correlations

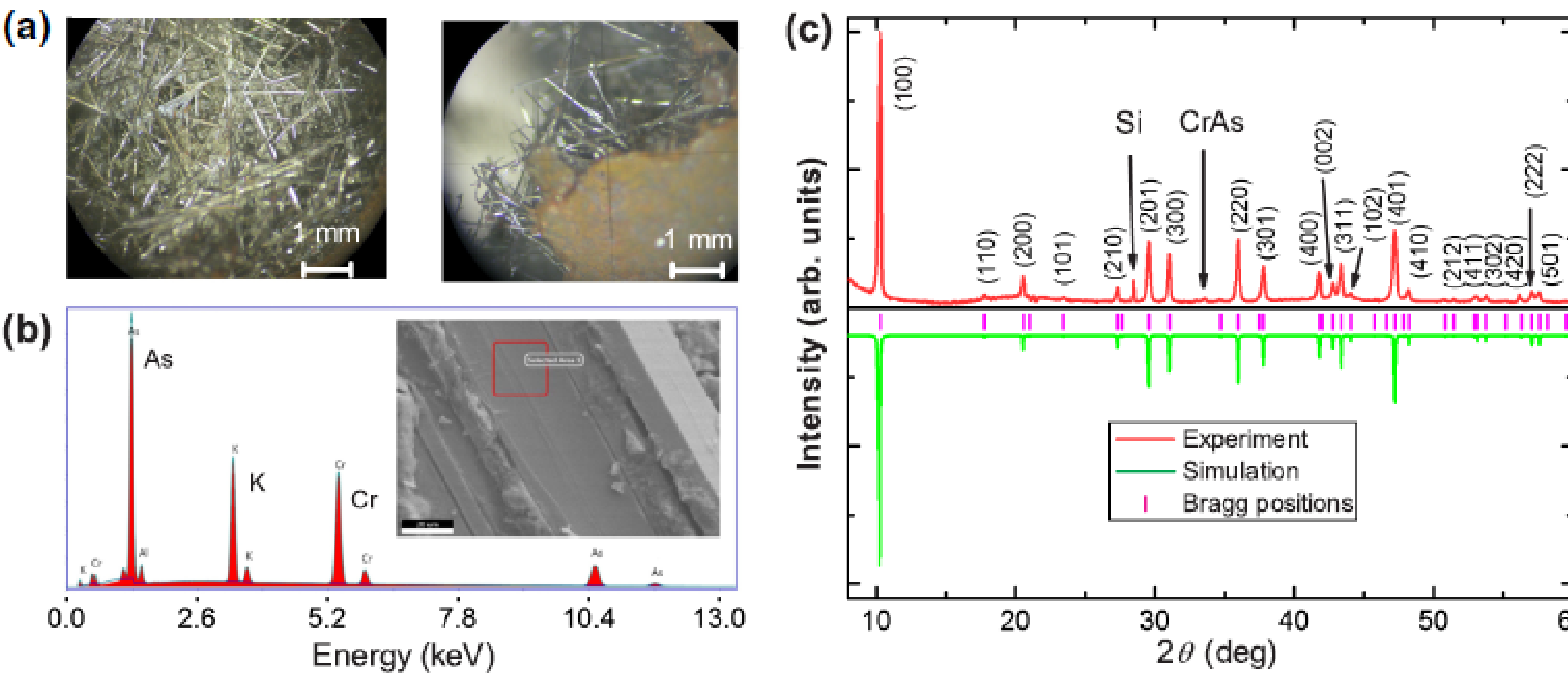
Jin-Ke Bao,[1] Ji-Yong Liu,[2] Cong-Wei Ma,[1] Zhi-Hao Meng,[1] Zhang-Tu Tang,[1] Yun-Lei Sun,[1] Hui-Fei Zhai,[1] Hao Jiang,[1] Hua Bai,[1] Chun-Mu Feng,[1] Zhu-An Xu,[1,3,4] and Guang-Han Cao[1,3,4,*]
[1]*Department of Physics, Zhejiang University, Hangzhou 310027, China*
[2]*Department of Chemistry, Zhejiang University, Hangzhou 310027, China*
[3]*State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, China*
[4]*Collaborative Innovation Centre of Advanced Microstructures, Nanjing 210093, China*
(Received 13 January 2015; published 9 February 2015)

Ambient-pressure SC at 6.1 K in Q1D $K_2Cr_3As_3$

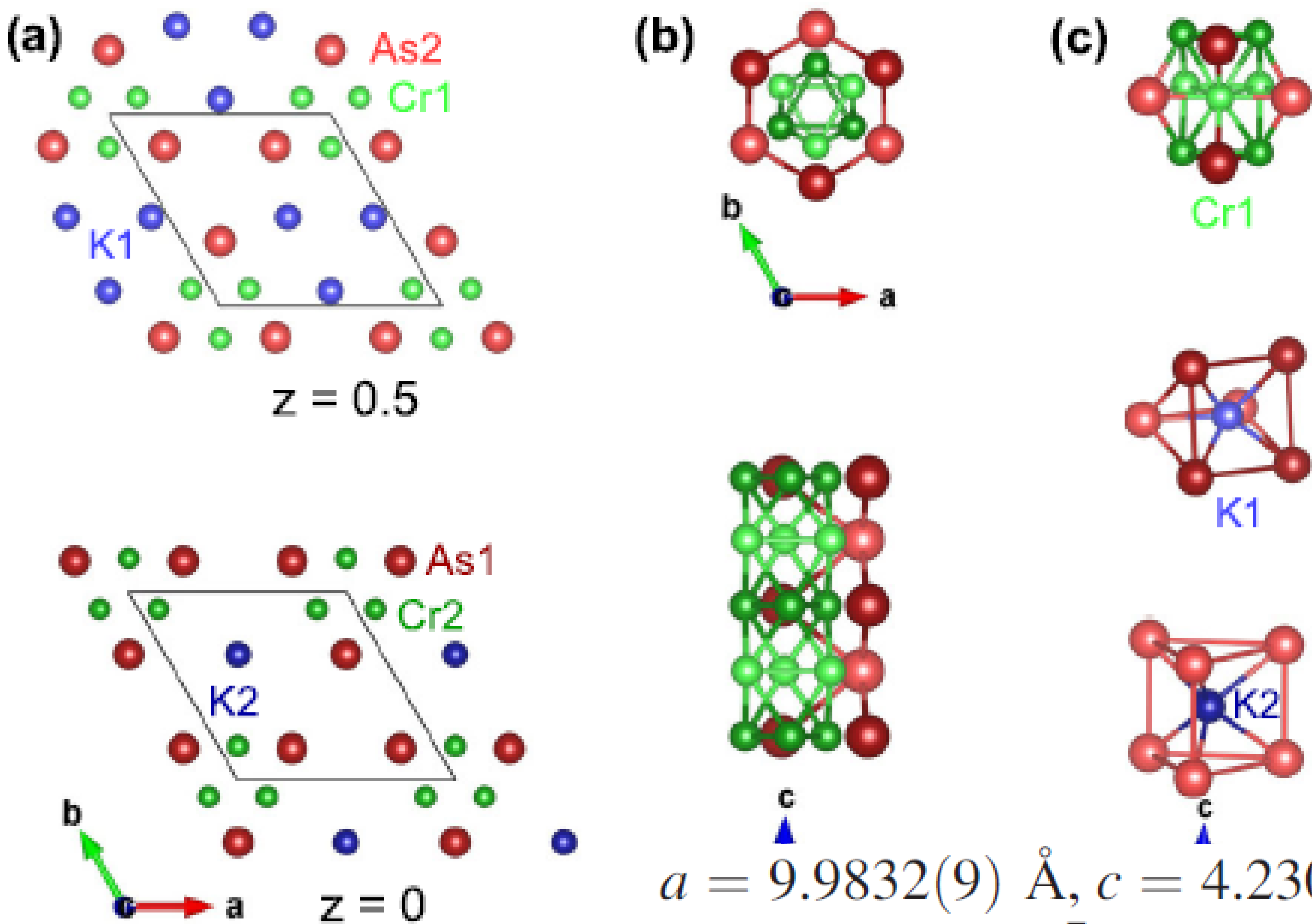


How could we discover it?

- SC in CrAs under HP
- (Ba,K)Cr_2As_2: "KCr_2As_2"?
- Unexpectedly, → $K_2Cr_3As_3$
- Difficulties: Sample is very air sensitive!
- SXs growth; Structure determination; Measurements



The Crystal Structure containing Cr_3As_3 chains

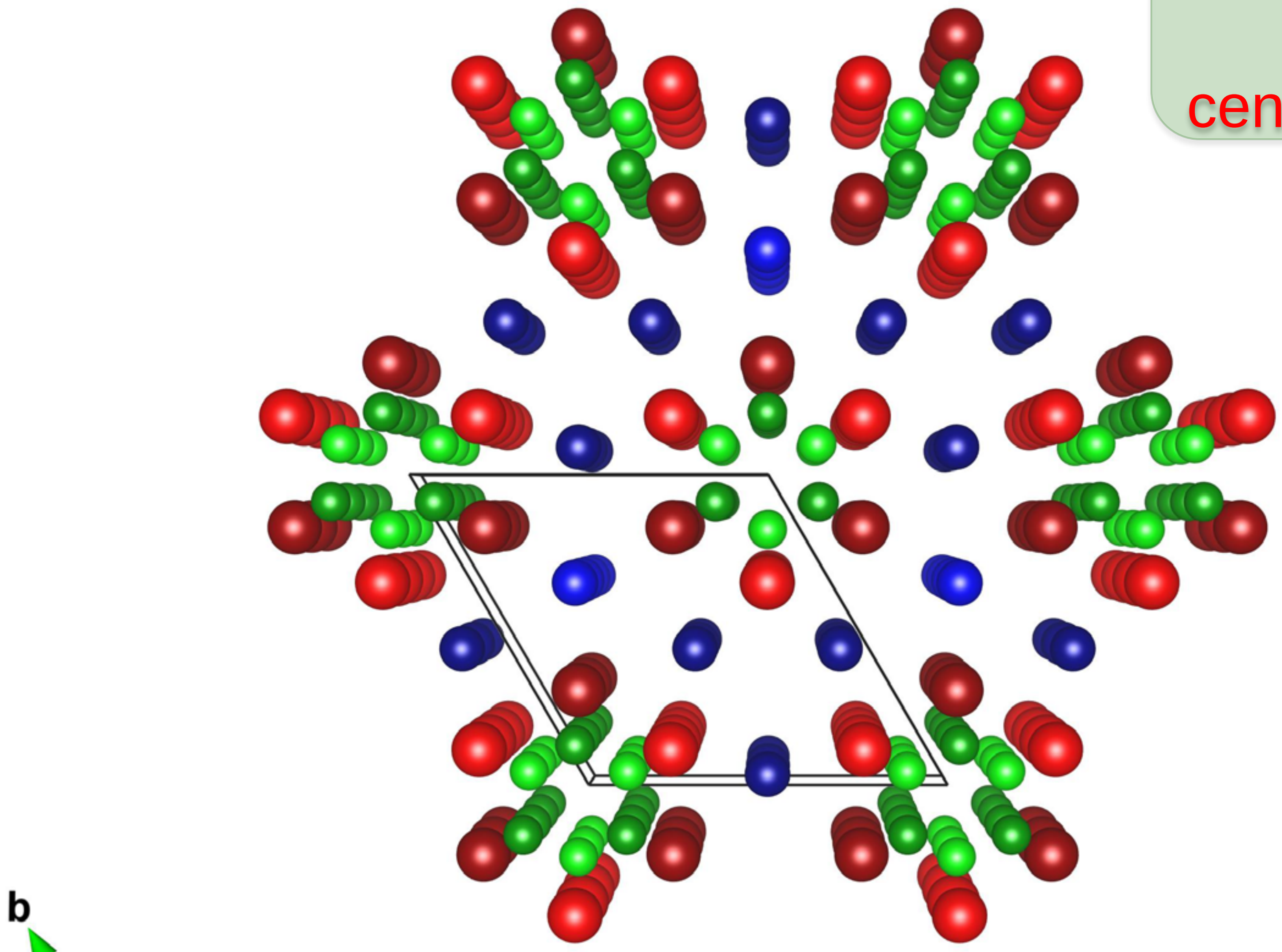


$a = 9.9832(9)$ Å, $c = 4.2304(4)$ Å

space group of $P\bar{6}m2$ (No. 187)

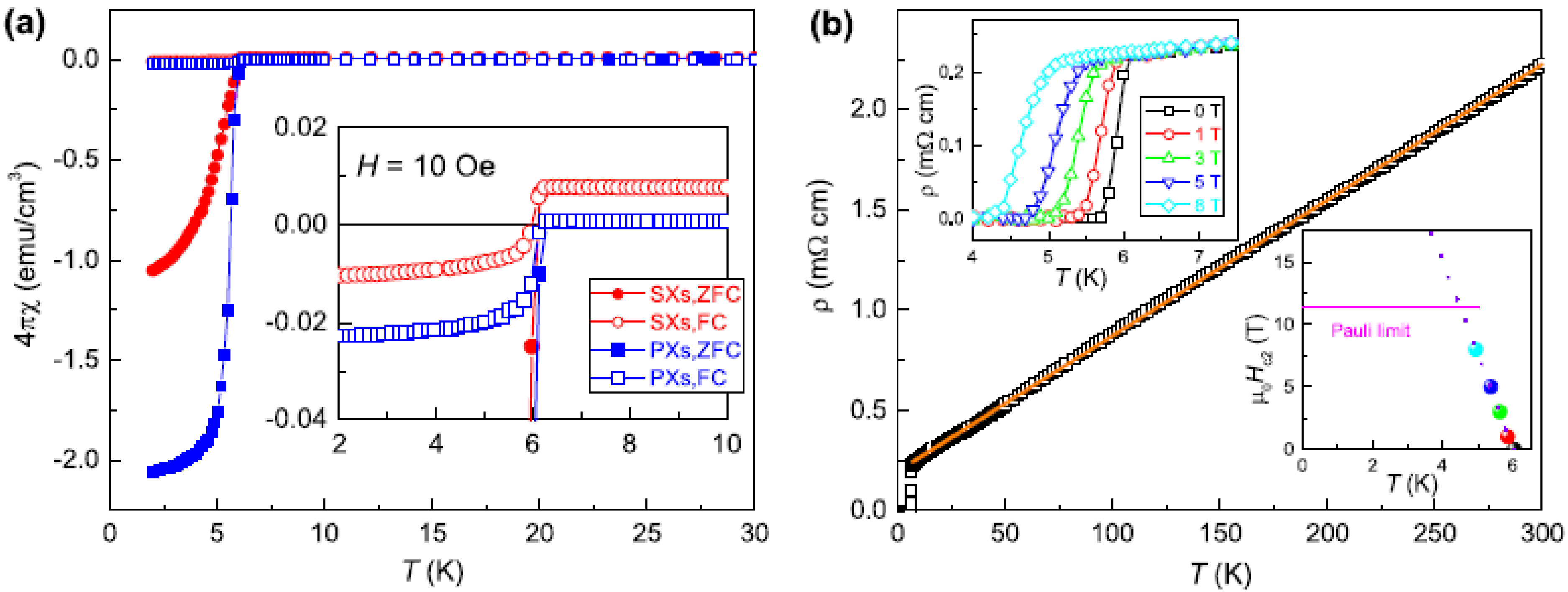
The Crystal Structure

SG: #187
PG: D_{3h}
non-centrosymmetric



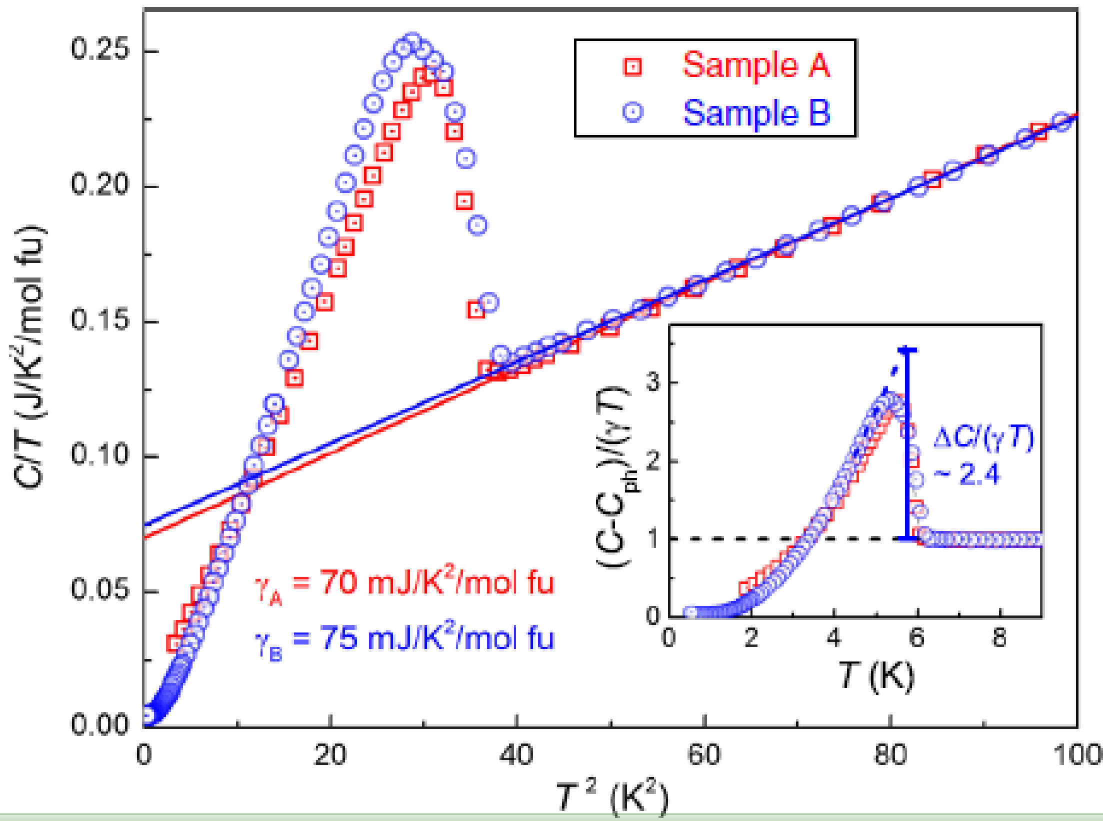
$a = 9.9832(9)$ Å, $c = 4.2304(4)$ Å
space group of $P\bar{6}m2$ (No. 187)

Ambient-pressure bulk SC at 6.1 K



- ➢Very high upper critical field: 3~4 H_P
- ➢Linear resistivity for polycrystalline samples (to be confirmed using well-protected SXs)

Specific-heat measurement of K233



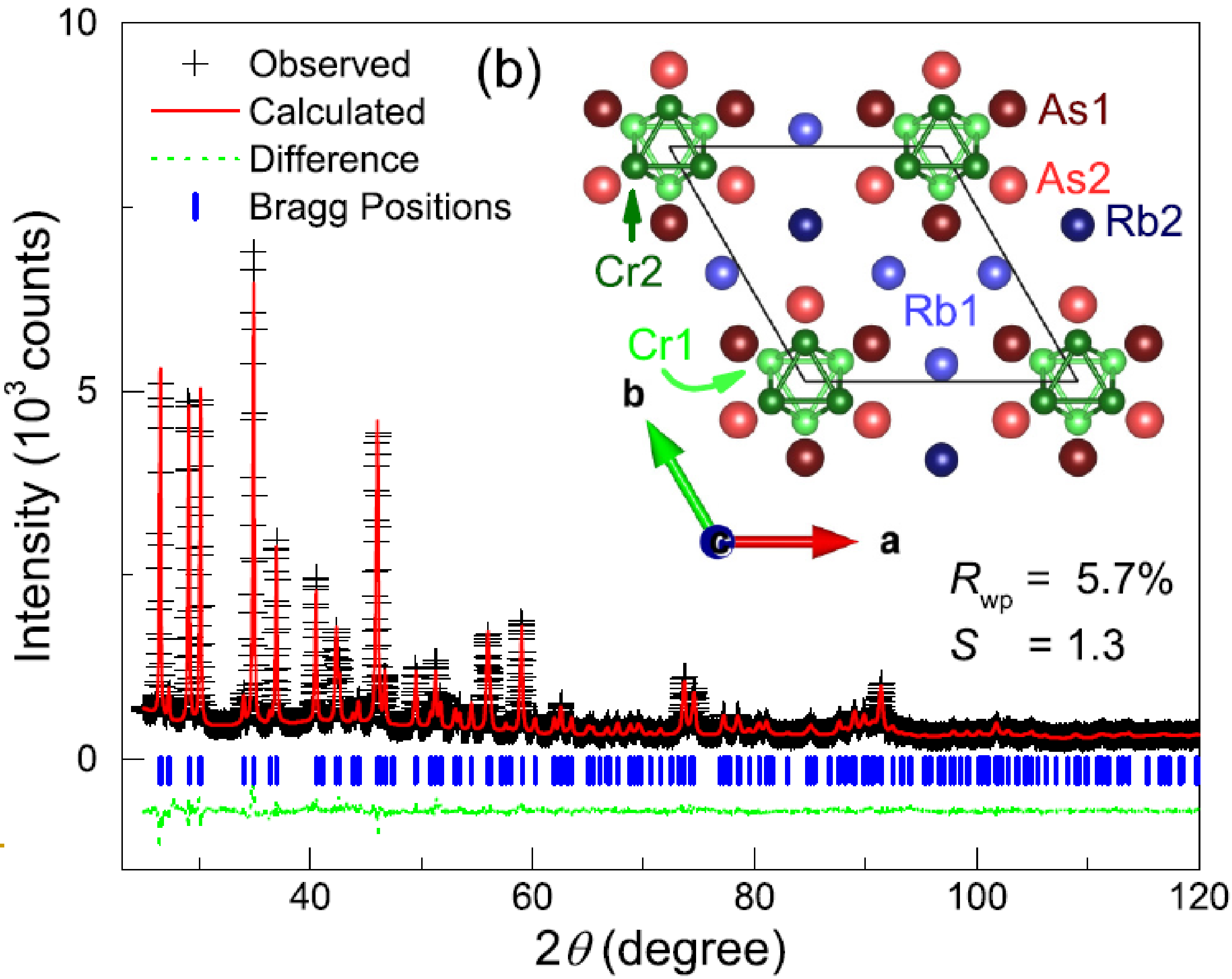
➢Large Sommerfeld coefficient:
 ~ 3-4 times of "bare" bandstructure DOS

➢T dependence is difficult due to the Schottky anomaly

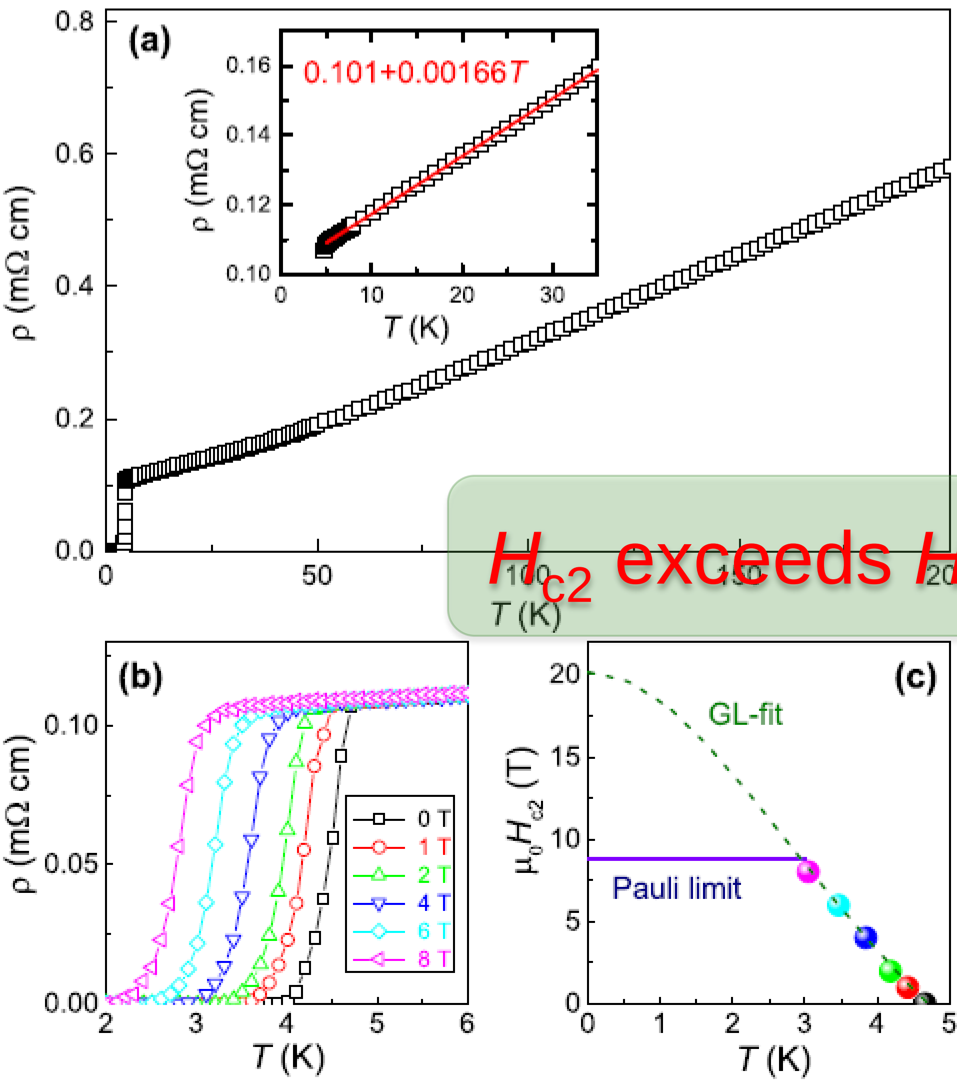
PHYSICAL REVIEW B **91**, 020506(R) (2015)

Unconventional superconductivity in quasi-one-dimensional $Rb_2Cr_3As_3$

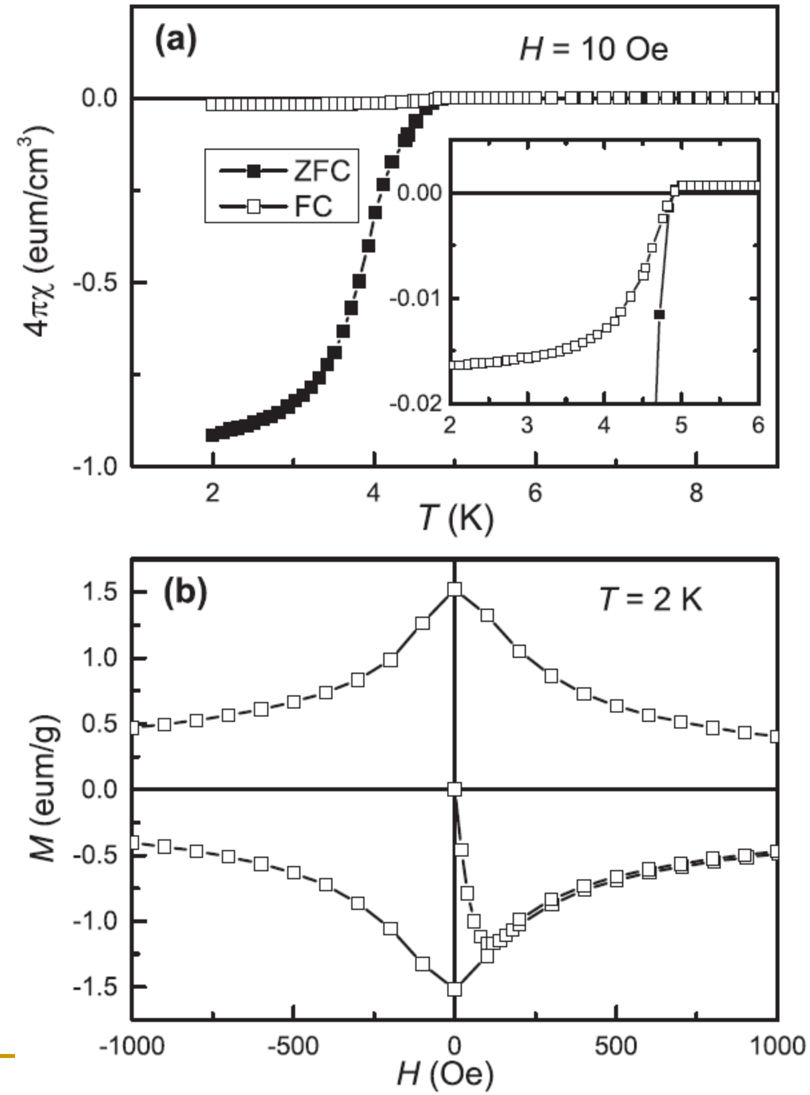
Zhang-Tu Tang,[1] Jin-Ke Bao,[1] Yi Liu,[1] Yun-Lei Sun,[1] Abduweli Ablimit,[1] Hui-Fei Zhai,[1] Hao Jiang,[1] Chun-Mu Feng,[1] Zhu-An Xu,[1,2,3] and Guang-Han Cao[1,2,3,*]



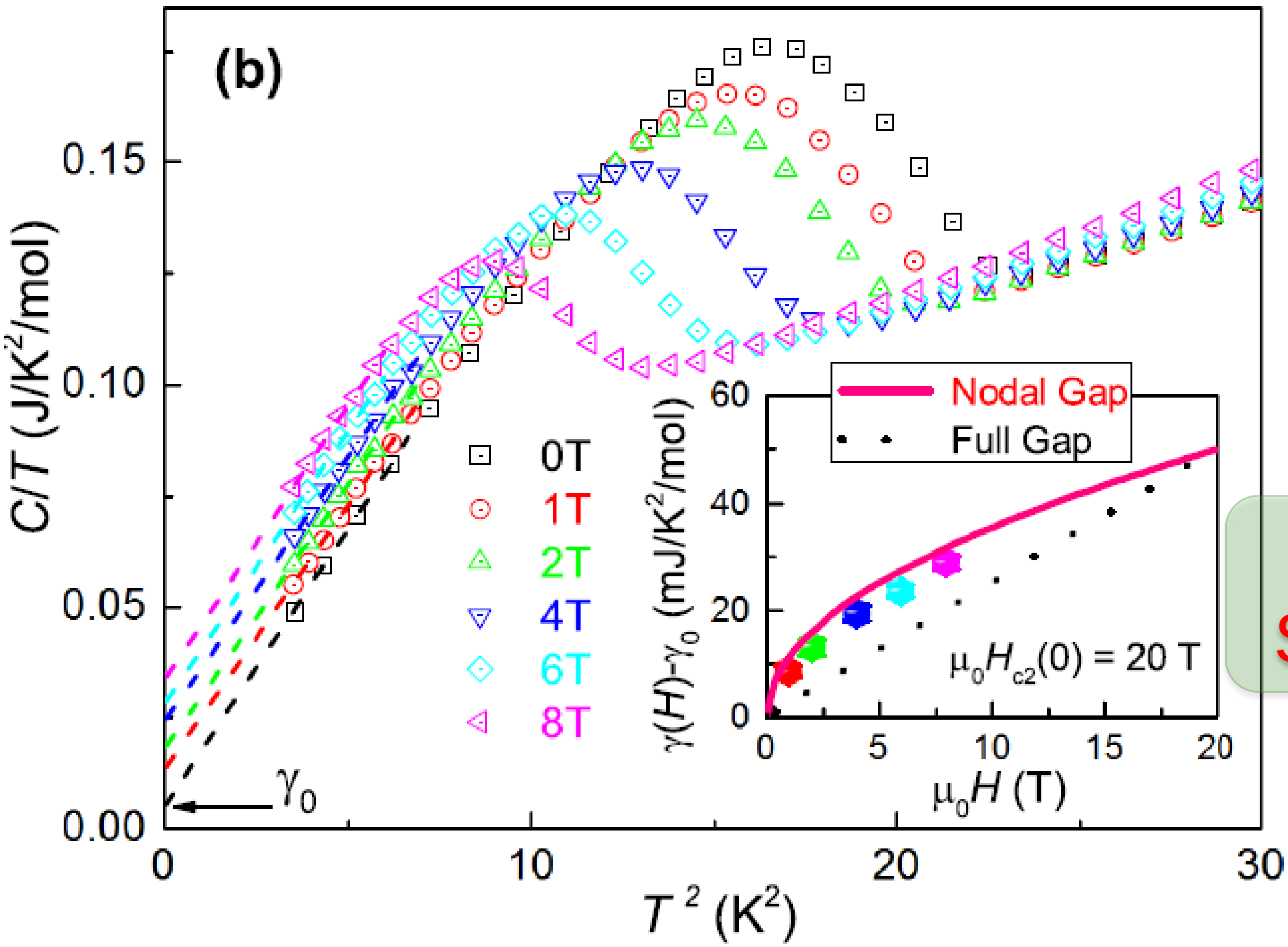
SC at 4.8 K in Rb233



H_{c2} exceeds H_P



Specific heat of Rb233



Existence of SC gap nodes

Superconductivity in quasi-one-dimensional $Cs_2Cr_3As_3$ with large interchain distance

SC at 2.2 K in Cs233

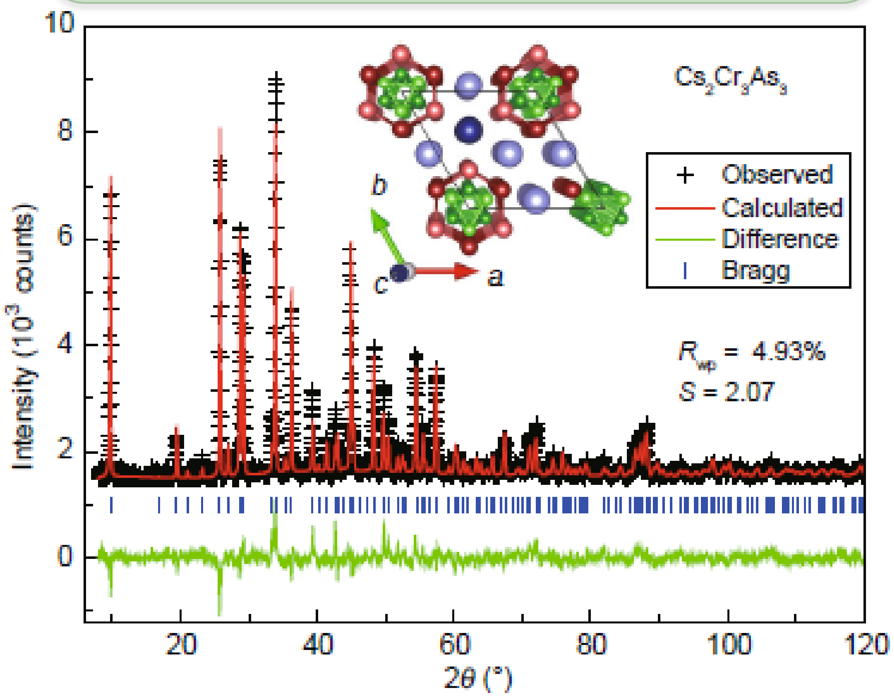
SCIENCE CHINA Materials

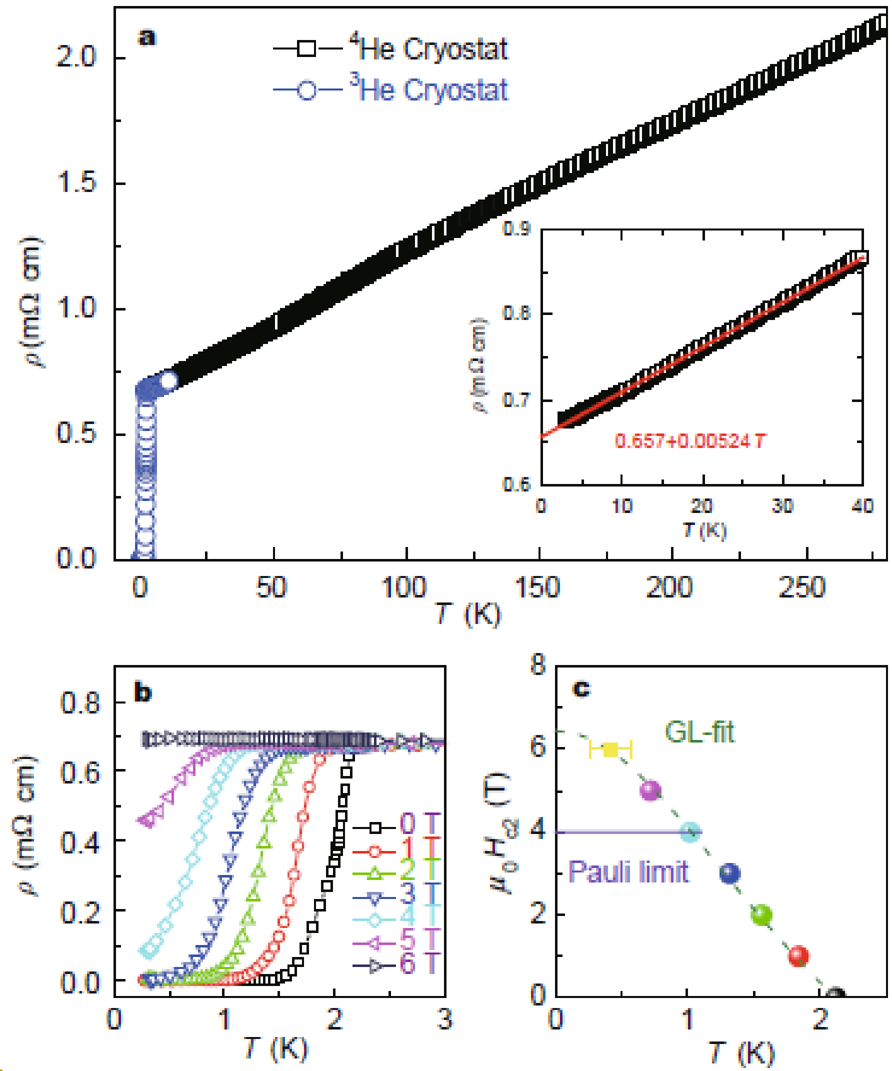
Published online 20 January 2015 | doi: 10.1007/s40843-015-0021-x

Sci China Mater 2015, 58: 16–20

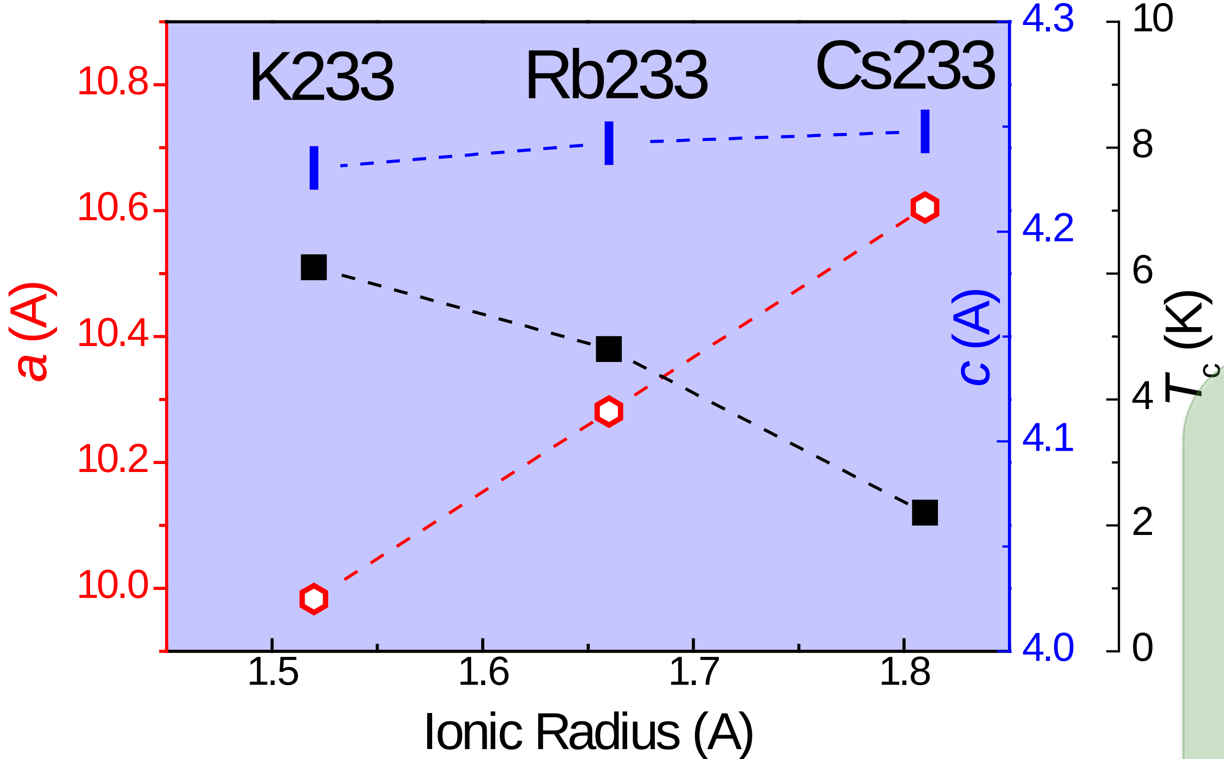
K→Rb→Cs: OK

→(Na, Li) unsuccessful





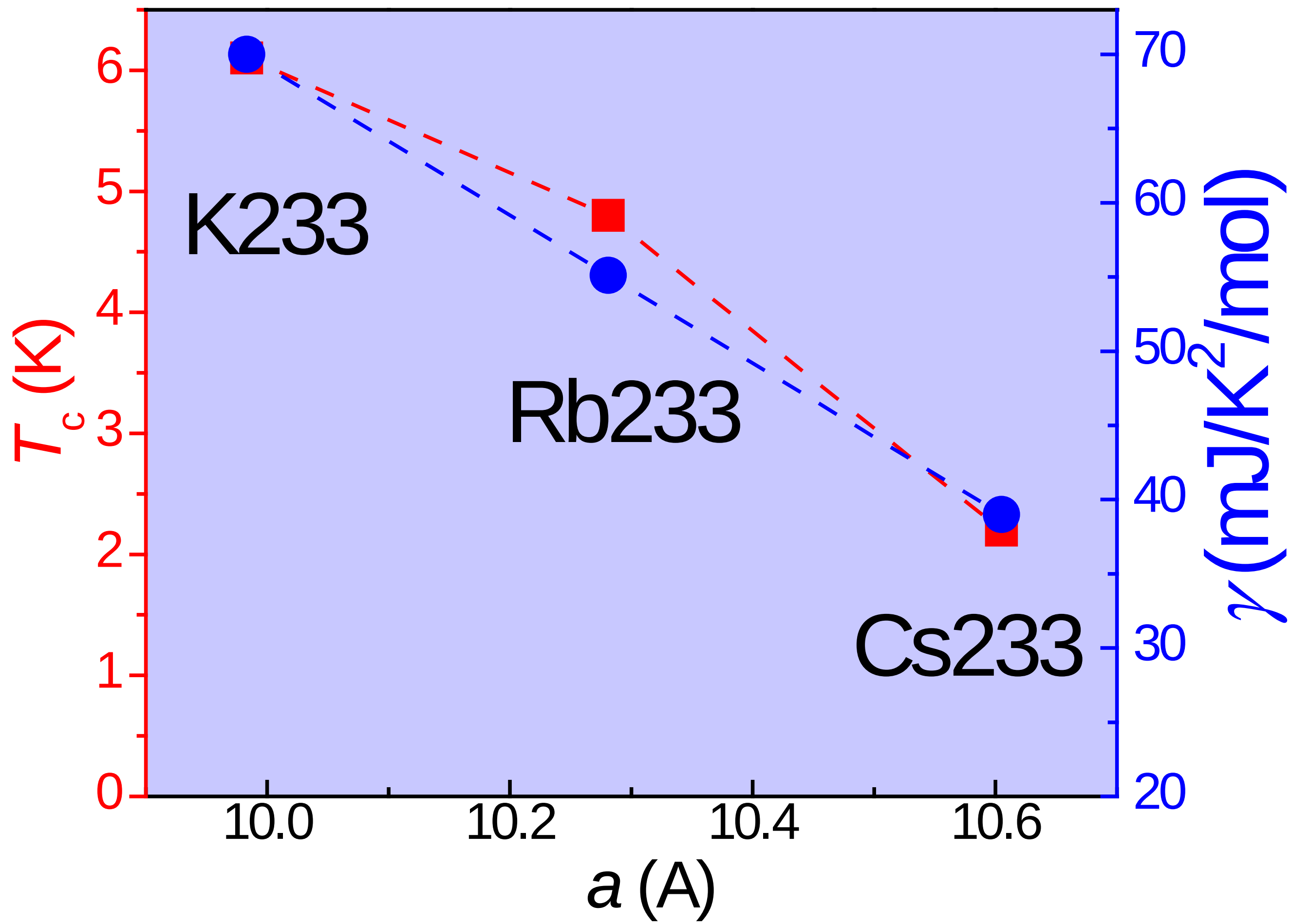
Influence of the ionic size of alkali metals



Implication:
Higher Tc in
Na233 & Li233
Or, under HP

Unfortunately,
Na233 & Li233
cannot be
synthesized,
HP supresses Tc
(arXiv1502.04304)

Correlation of T_c and Sommerfeld coefficient in A233

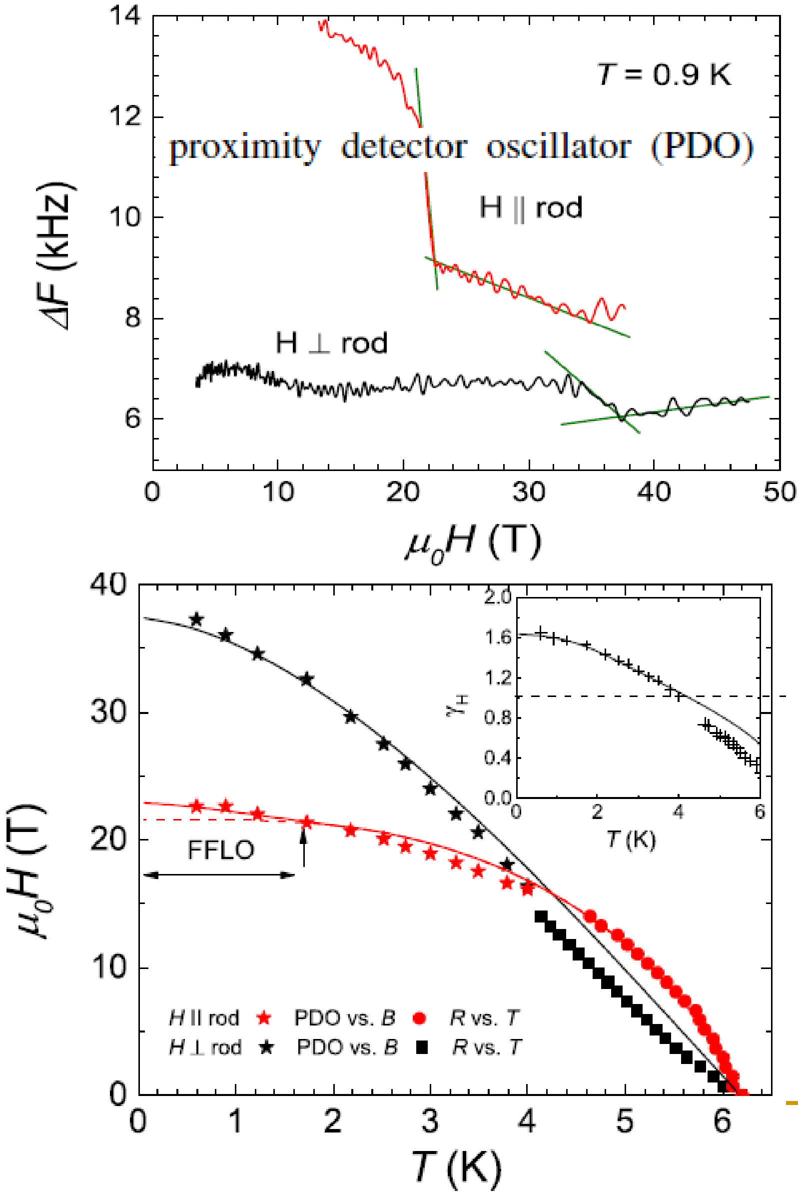


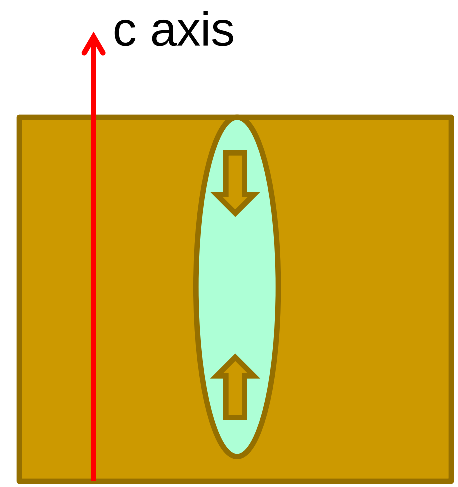
Theoretical and Experimental Progress

- **DFT calculations:** arXiv:1412.1309 and arXiv:1501.00412, CPL2015
- **Theory suggests an f-wave:** arXiv:1502.03928
- **Theory suggests a p_z-wave:** arXiv:1503.06707
- **Theory again suggests spin-triplet instabilities: arXiv: 1503.08965**
- **Recent DFT calculations suggest e-ph SC: arXiv: 1508.0082**

- **NMR/NQR :** arXiv:1501.00713, PRL2015 and arXiv: 1508.01012 (Rb233)
- **Penetration depth :** arXiv:1501.01880, PRB2015
- **Anisotropy reversal of Hc2: arXiv: 1505.05547,PRB2015**
- **muSR: arXiv:***1505.05743*

F. F. BALAKIREV *et al.*
PHYSICAL REVIEW B **91**, 220505(R) (2015)

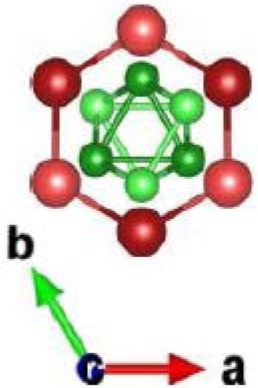




Spin-singlet
Cooper pairs

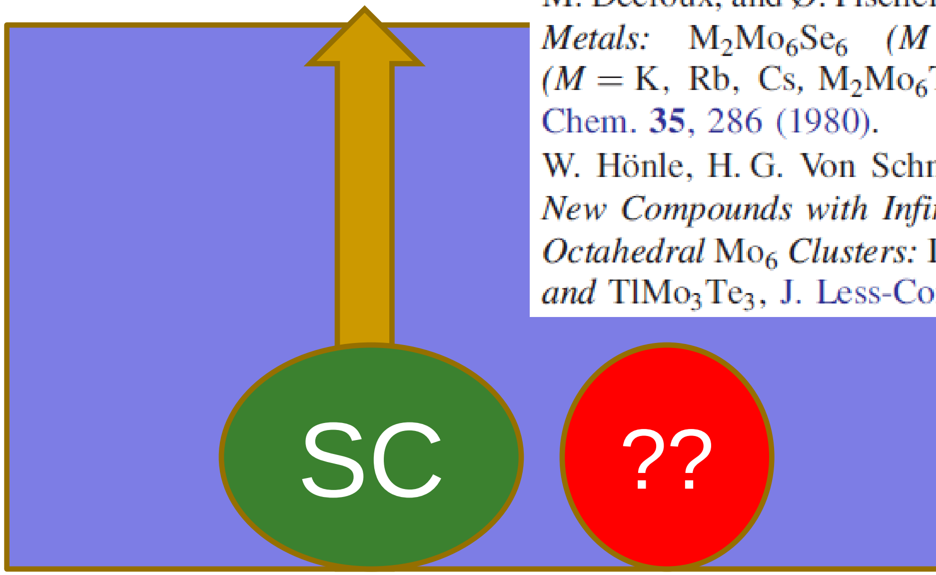
Pauli limiting for H//rod

Change in Cr valence in Cr_3As_3-based mater.?



M. Potel, R. Chevrel, M. Sergent, J.C. Armici, M. Decroux, and Ø. Fischer, *New Pseudo-One-Dimensional Metals:* $M_2Mo_6Se_6$ *(M* = Na, In, K, Tl, $M_2Mo_6Se_6$ *(M* = K, Rb, Cs, $M_2Mo_6Te_6$ *(M* = In, Tl*)*, J. Solid State Chem. **35**, 286 (1980).

W. Hönle, H. G. Von Schnering, A. Lipka, and K. Yvon, *New Compounds with Infinite Chains of Face-Condensed Octahedral* Mo_6 *Clusters:* $InMo_3Se_3$, $InMo_3Te_3$, $TlMo_3Se_3$ *and* $TlMo_3Te_3$, J. Less-Common Met. **71**, 135 (1980).



AMo_3Se_3

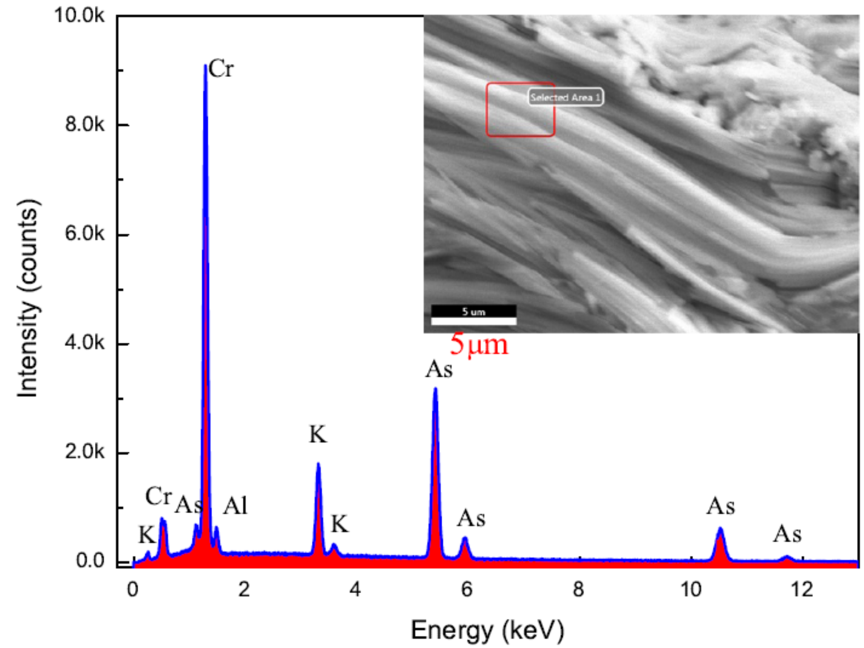
Cr valence	2.33+	2.67+
3d-electron Nr	3.67	3.33

K233 → K133 ?

Absence of bulk SC in KCr_3As_3

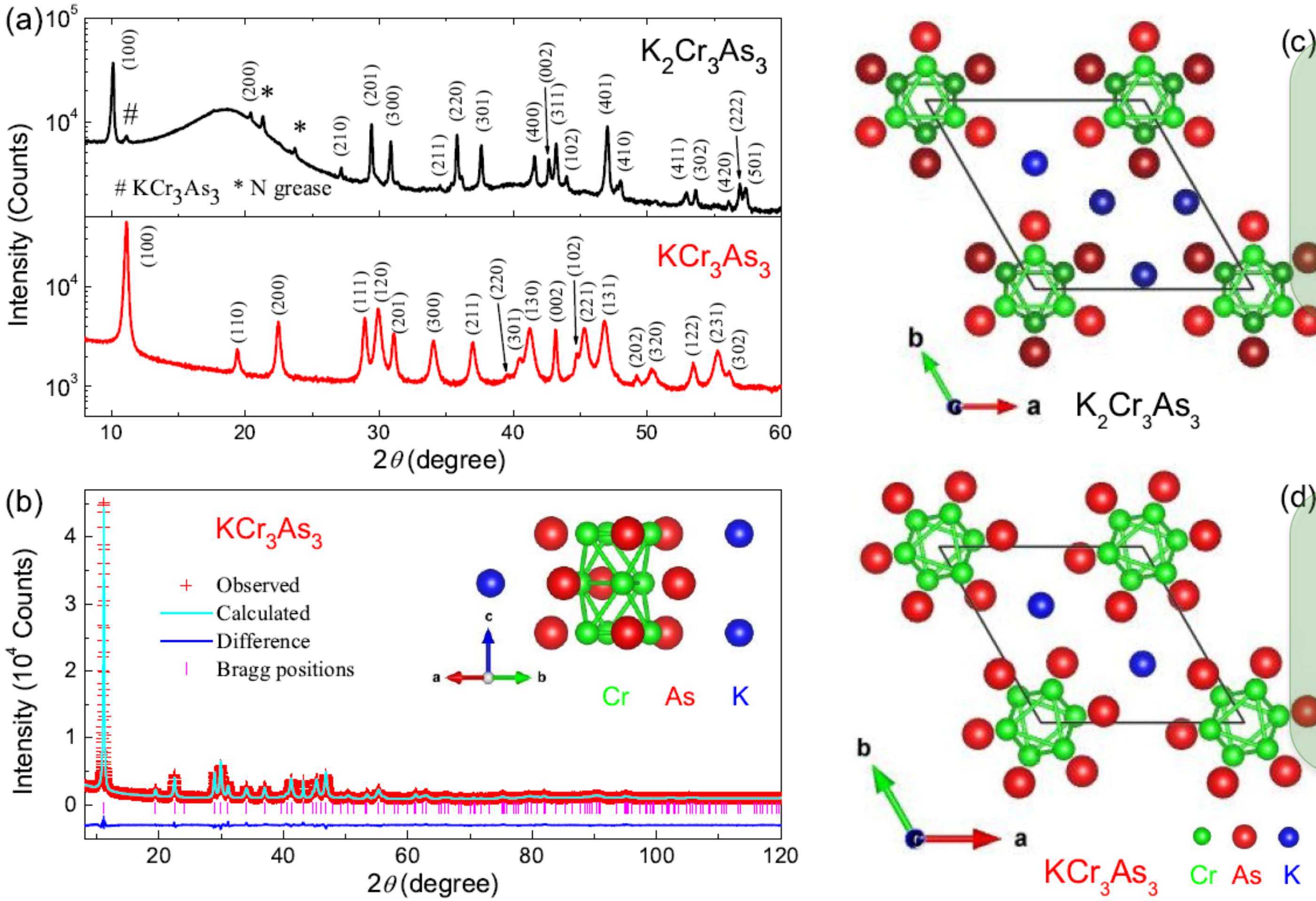
$$K_2Cr_3As_3 + C_2H_5OH \rightarrow KCr_3As_3 + KOC_2H_5 + \frac{1}{2}H_2\uparrow$$

$A_2Cr_3As_3$ ACr_3As_3



Crystal structure of K133

ACr_3As_3 isostructural to AMo_3Se_3



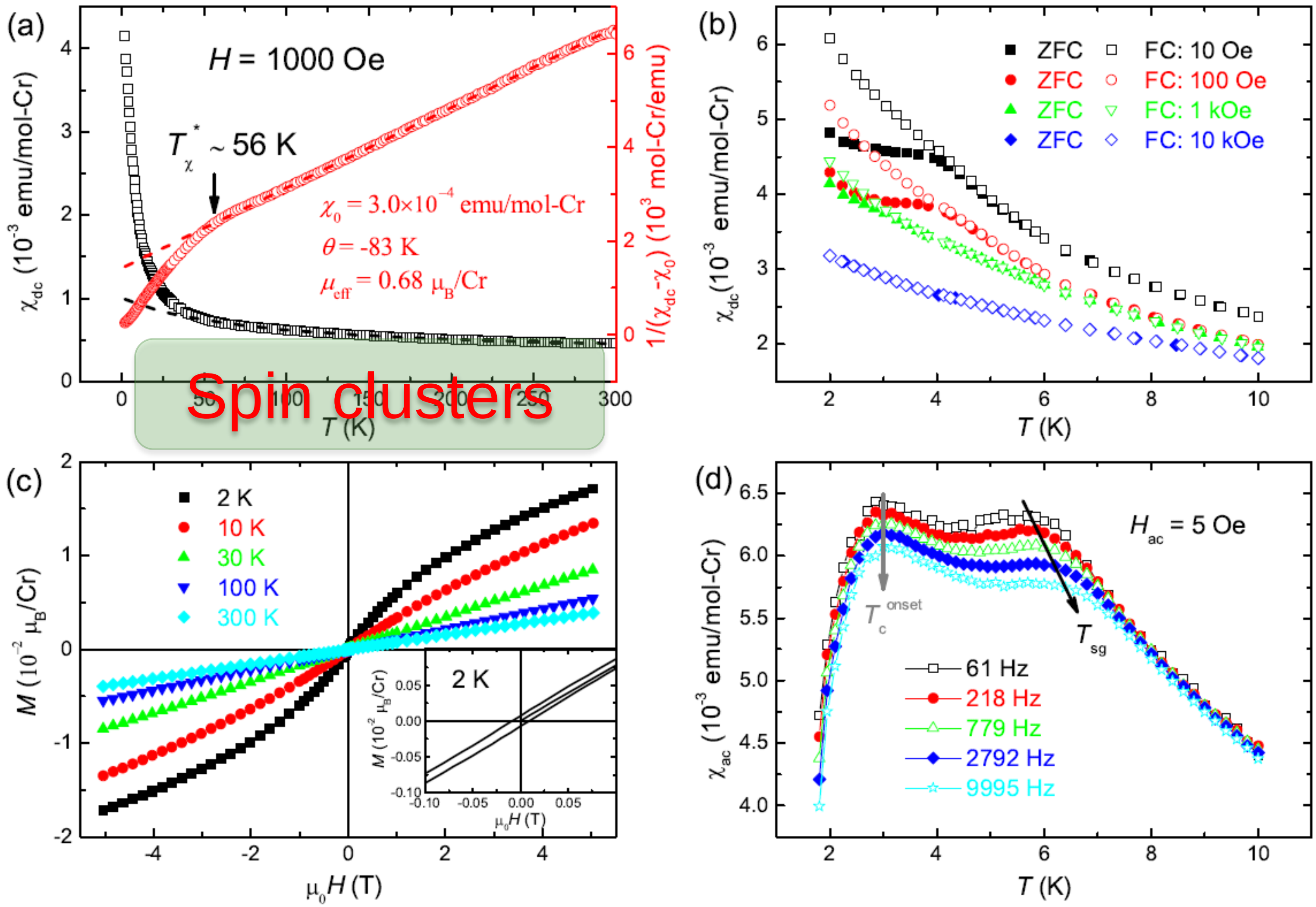
SG: #187
PG: D_{3h}
non-centrosymmetric

SG: #176
PG: C_{6h}
centrosymmetric

Magnetic properties of K133

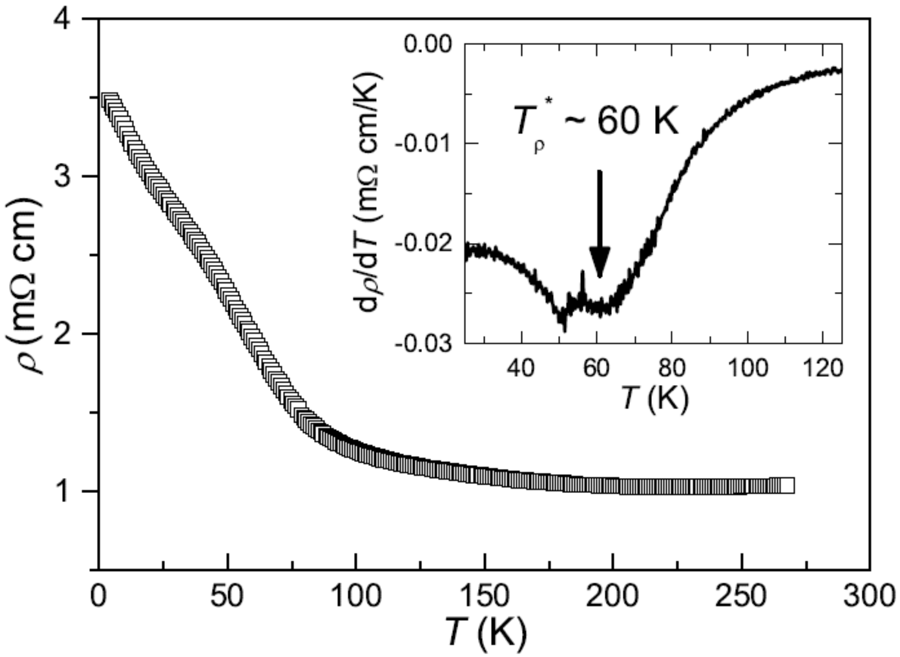
Local moment appears

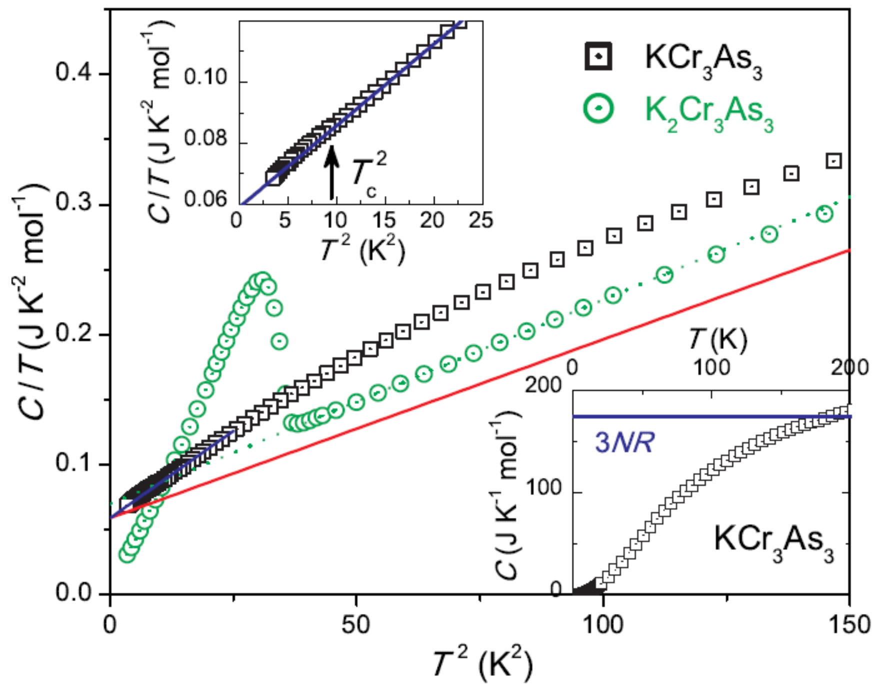
Spin clusters freeze



Spin clusters

Resistivity **K133** Specific heat

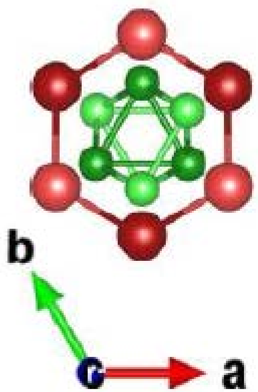


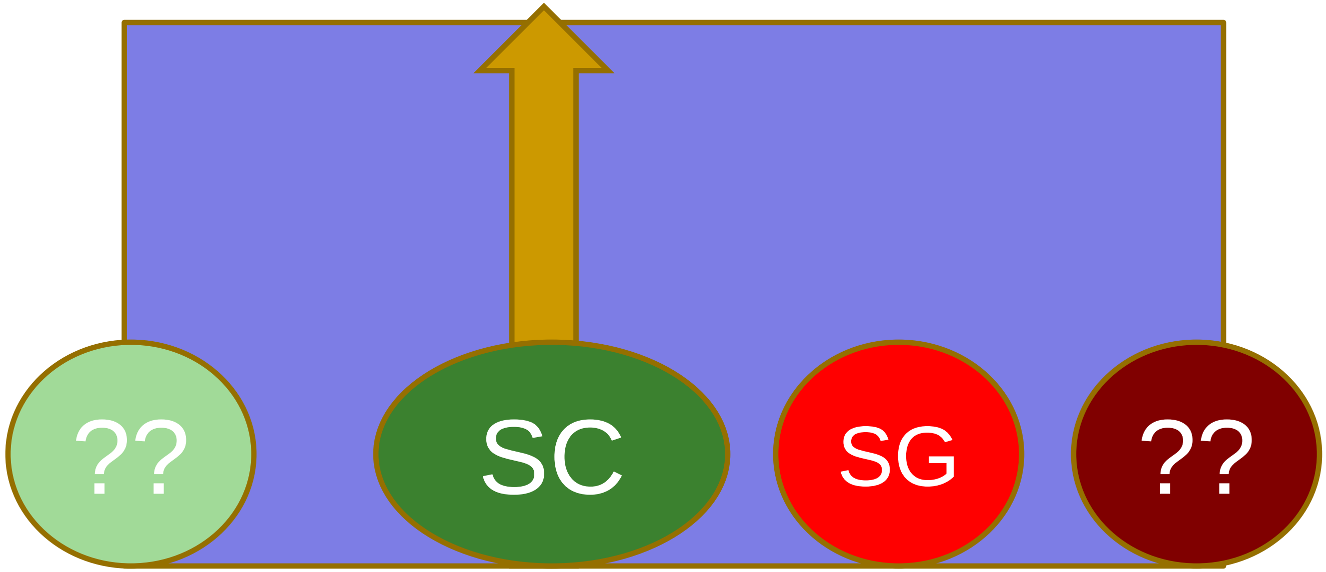


Enhanced magnetic scattering around 60 K?

- absence of bulk SC
- C_p from spin glass
- Metallic: γ~60 mJ/K²/mol

Change in Cr valence in Cr_3As_3-based mater.?





Cr valence	2+	2.33+	2.67+	3+
3d-electron Nr	4	3.67	3.33	3

K333 → K233 → K133 → 33

Concluding Remarks & Open Questions

- **First Cr-based SC family at ambient pressure**
  - **→More members? Higher Tc?**
  - **→Mn-based SC (Mn-P superconducts at HP as well)**
- **Unusual normal-state and superconducting properties**
  - **→Unconventional SC; pairing symmetry?**
- **Quasi-1D crystal structure**
  - **→Possible Tomonaga-Luttinger liquid in 233 and 133?**
- **Why SC is absent in 133?**

1) Change of FSs due to "hole doping"
2) Weakened interchain coupling due to loss of K1
3) Anderson localizations kill SC?
4) Cluster spin glass due to geometrical frustration?

- ➢ Why large and anisotropic H_{c2}?
- ➢ What is the NS? A Luttinger liquid?
- ➢ FM spin fluctuations?
- ➢ Nodal SC?
- ➢ Triplet pairing?
- ➢ p or f wave?
- ➢ ……

32 class of SCs categorized in terms of “conventionality”

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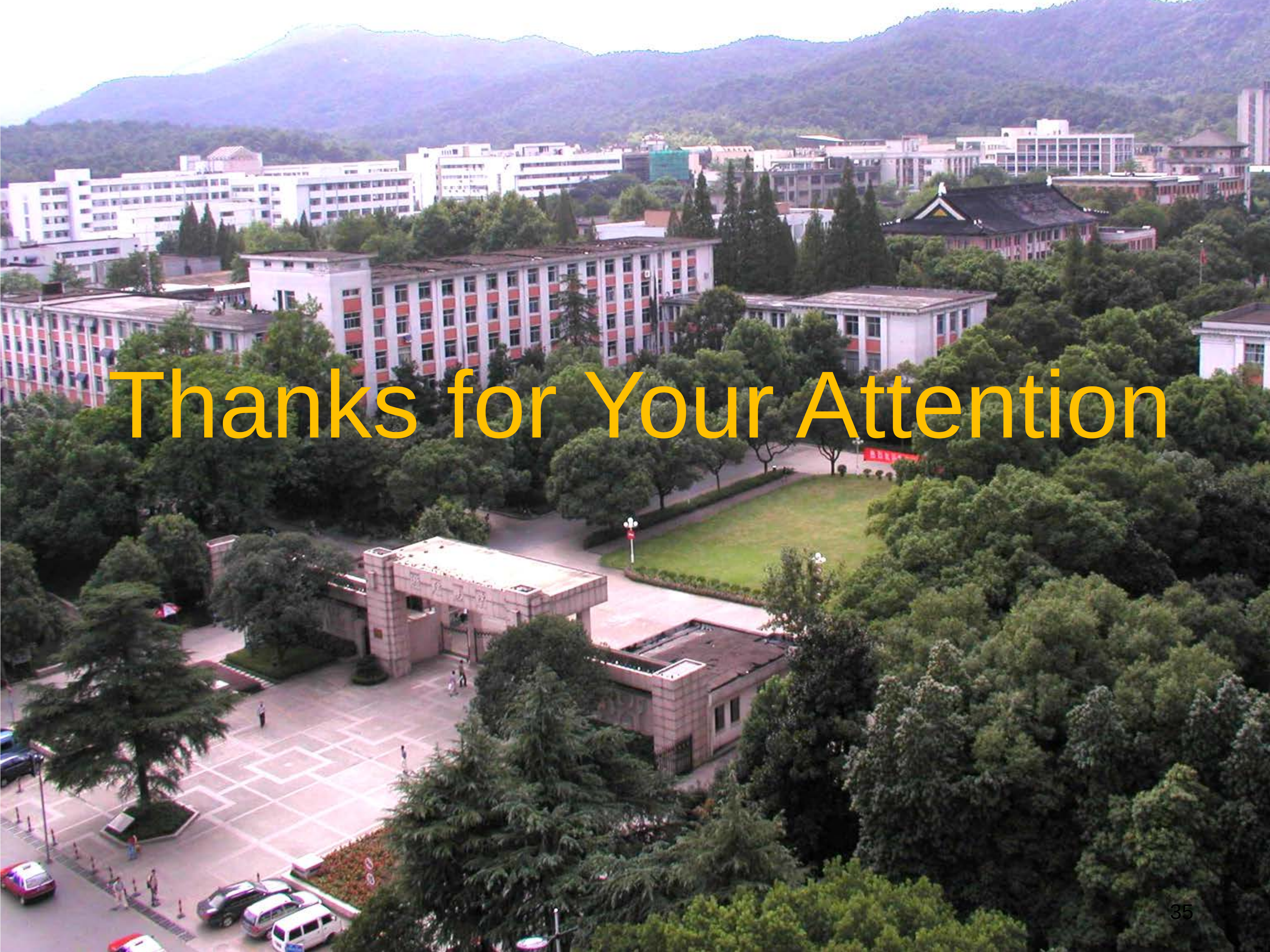
Hirsch, Maple & Marsiglio

Superconducting materials classes: Introduction and overview

	Material class	Year	Max T_c material	T_c^{max} (K)	ξ (Å)	λ_L (Å)	$2\Delta/k_BT_c$	dT_c/dP	mag?	dim	symm	Category
C1	Elements,	1911	Nb	9.5	380	390	3.80	+/−	n	3	s	conv
	alloys and simple compounds	1912	NbN	17	50	2000	4.1	+/−	n	3	s	conv
C2	A15’s	1954	Nb_3Ge	23.2	55	1000	4.2	+	n	3	s	conv
C3	Doped semiconductors	1964	CB_x	10	950	720	3.5	−	n	3	s	conv
C4	Insul. elements under pressure	1964	S	17				+	n	3	s	conv
C5	Intercalated graphite	1965	C_6Ca	11.5	380	720	3.6	+	n	2	s	conv
C6	Metallic elements under pressure	1968	Ca	25				+/−	n	3	s	conv
C7	Hydrogen-rich materials	1970	PdD	10.7	400		3.8	+/−	n	3	s	conv
C8	Layered t. m. dichalcogenides	1970	NbS_2	7.2	100	1250	3.7	−	n	2	s	conv.
C9	Chevrel phases	1971	$PbMo_6S_8$	15	30	3000	4.7	+/−	y	3	s	conv
C10	Magnetic superconductors	1972	$ErRh_4B_4$	8.7	180	830	4	+/−	y	3	s	conv
C11	Thin films	1978							n	2	s	conv
C12	Magnesium diboride	2001	MgB_2	39	52	1400	4.5	−	n	2	s	conv
P1	Bismuthates	1975	$Ba_{1-x}K_xBiO_3$	34	50	5500	4	−	n	3	s	poss unc
P2	Fullerenes	1991	$RbCs_2C_{60}$	33	30	4500	3.5–5.0	−	n	0	s	poss unc
P3	Borocarbides	1993	$YPd_5B_3C_{0.3}$	23	100	1000	4	+/−	y,n	2	s + g?	poss unc
P4	Plutonium compounds	2002	$PuCoGa_5$	18.5	16	2400	5–8	+/−	y	2	*d*	poss unc
P5	Interface superconductivity	2007	$LaAlO_3/SrTiO_3$	.35	600				y	2		poss unc
P6	Aromatic hydrocarbons	2010	K-doped DBP	33	180	770		+/−	n	3		poss unc
P7	Doped top. ins.	2010	$Cu_x(PbSe)_5(Bi_2Se_3)_6$	3	110	13000			n	2		poss unc
P8	BiS_2-based materials	2012	$YbO_{0.5}F_{0.5}BiS_2$	5.4	53	5000	7.2	+/−	n	2	s	poss unc

U12 alkali chromium arsenides?

	Material class	Year	Max T_c material	T_c^{max} (K)	ξ (Å)	λ_L (Å)	$2\Delta/k_BT_c$	dT_c/dP	mag?	dim	symm	Category
U3	Cuprates hole-doped	1986	$HgBa_2Ca_2Cu_3O_9$	134	20	1200	4.3	+	y	2	*d*	unconv
U4	Cuprates e-doped	1989	$Sr_{0.9}La_xCuO_2$	40	50	2500	3.5	−	y	2	*d*	unconv
U5	Strontium ruthenate	1994	Sr_2RuO_4	1.5	660	1500		−	y	2	*p*	unconv
U6	Layered nitrides	1996	Ca(THF)HfNCl	26	60	4700	2.9–10	−	n	2	*d + id*	unconv
U7	Ferromagnetic sc	2000	UGe_2	0.8	100	$\sim 10^4$		+/−	y	3	p	unconv
U8	Cobalt oxyde hydrate	2003	$Na_x(H_3O)_zCoO_2{\cdot}yH_20$	4.7	100	7000	4.3–4.6	−	y	2	?	unconv
U9	Non-centro-symmetric	2004	$SrPtSi_3$	2	60	8000			y	3	s/p	unconv
U10	Iron pnictides	2008	$SmFeAsO_{0.85}$	55	10–50	2000	7.5	+/−	y	2	s±	unconv
U11	Iron chalcogenides	2008	$Na_xFe_2Se_2$	46	20	2000	3.8	+	y	2	s	unconv


Thanks for Your Attention