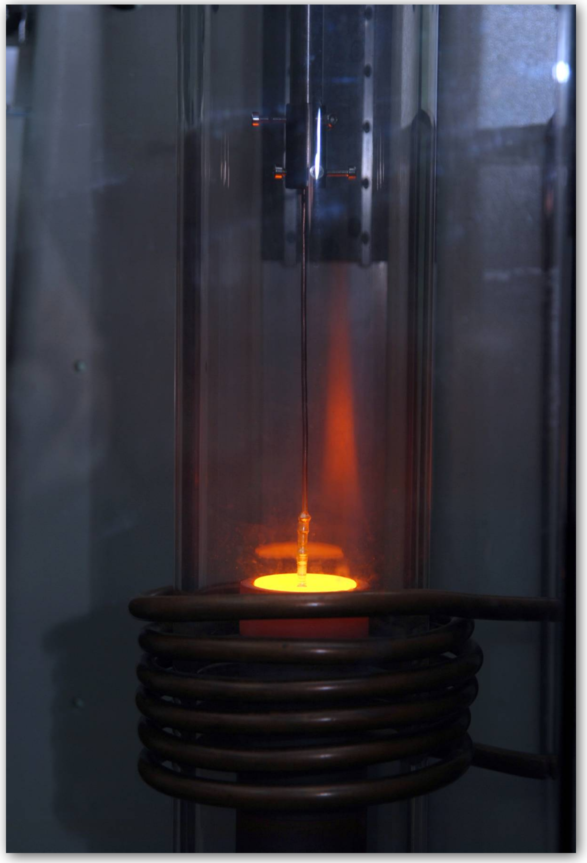
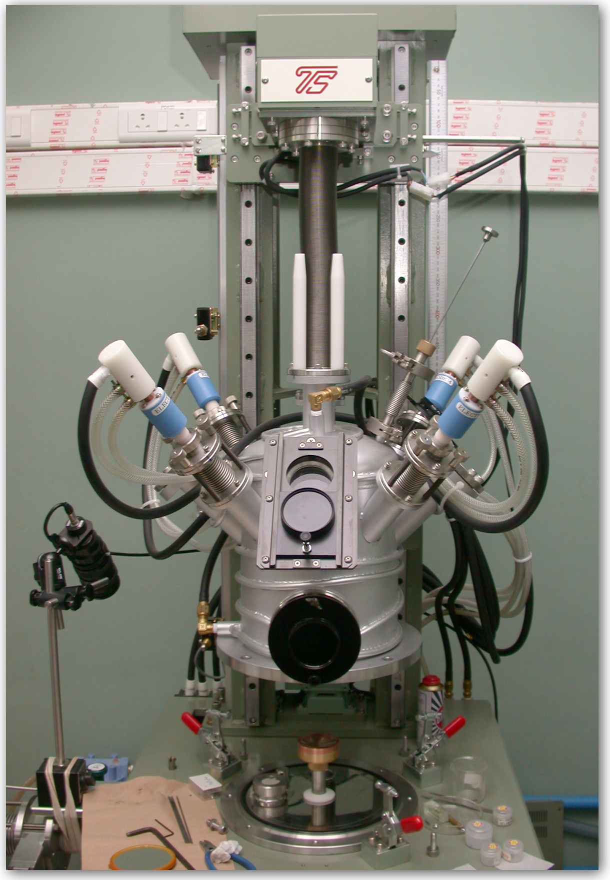
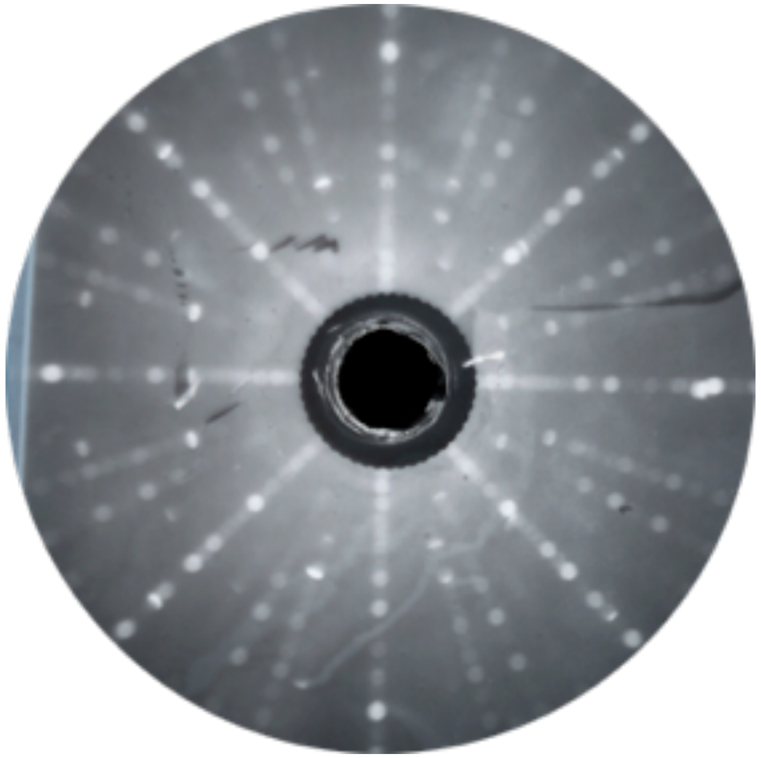
Crystal growth of rare-earth intermetallics and pnictide superconductors

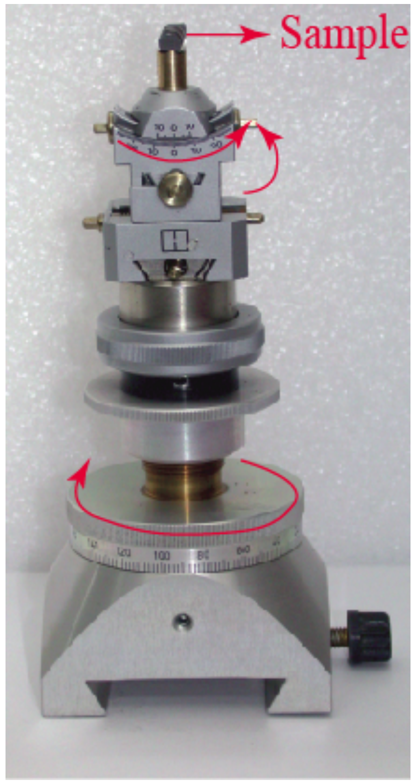






Dr. A. Thamizhavel

DCMPMS, TiFR



Outline of my talk

Various crystal growth methods to grow metallic crystals

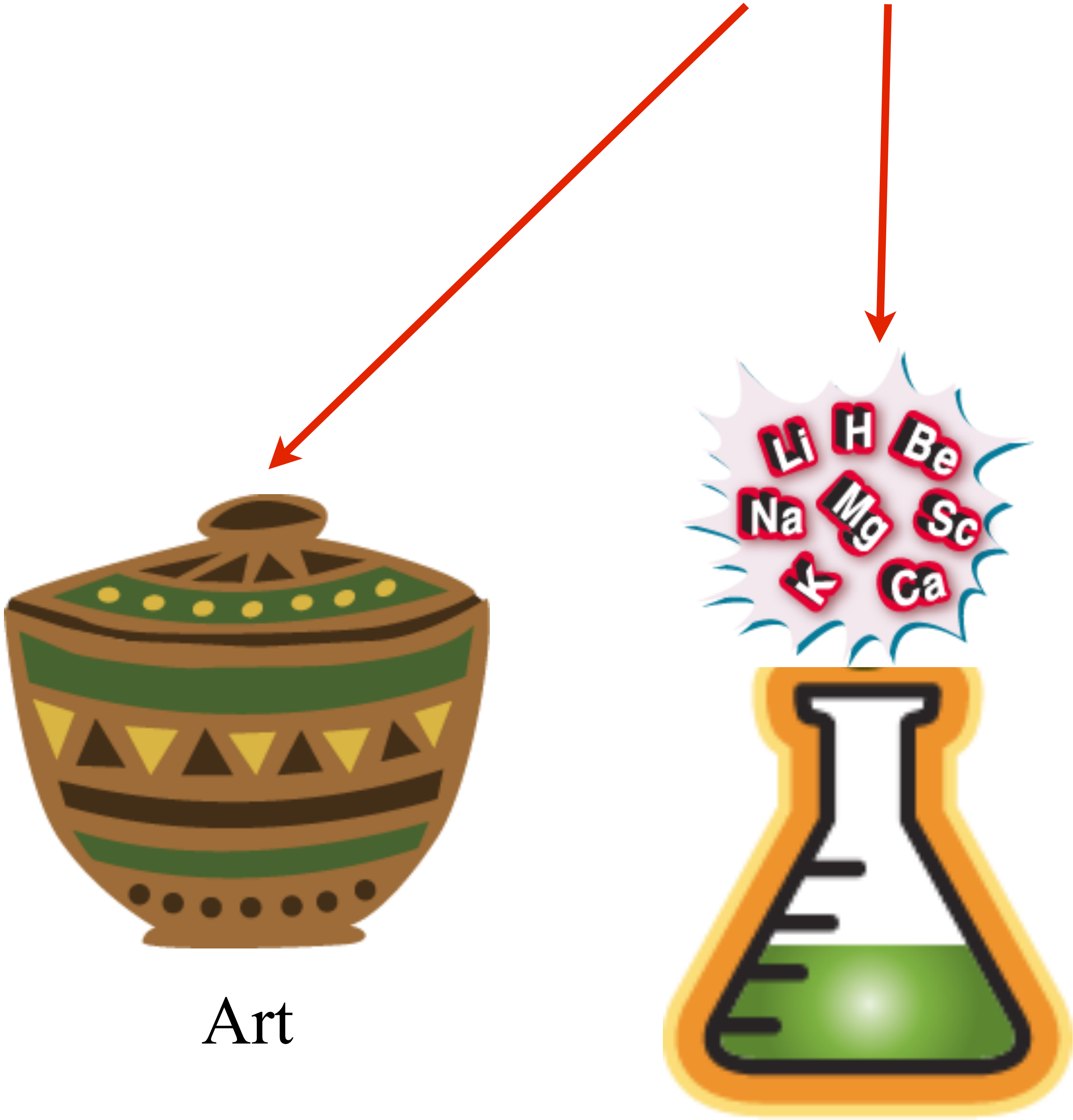
Crystal growth and superconducting properties of $CaFe_{2-x}T_xAs_2$ (T = Co and Ni) single crystals

Crystal Growth

Crystal Growth

Art

Crystal Growth



Art

Science

Crystal Growth

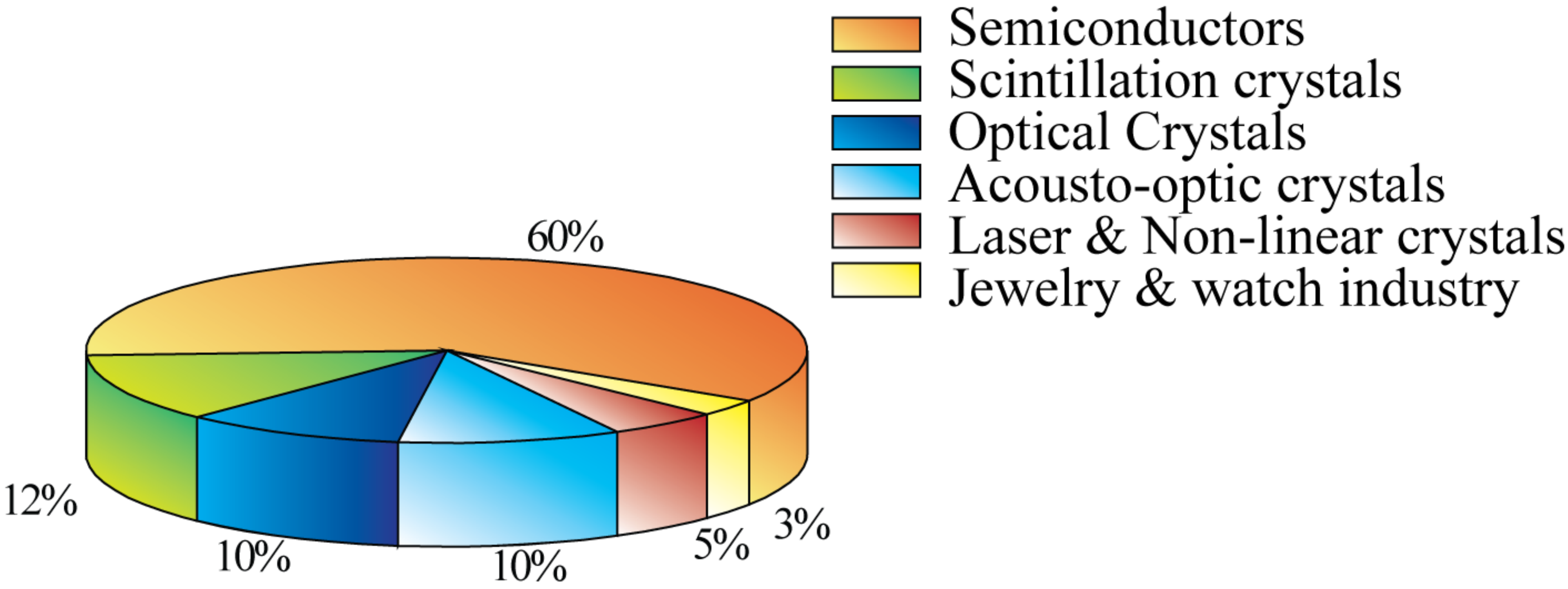
Art

Science

300mm Silicium Cz crystal with a mass of 250kg, form a 32" crucible (source Wacker Siltronic AG)

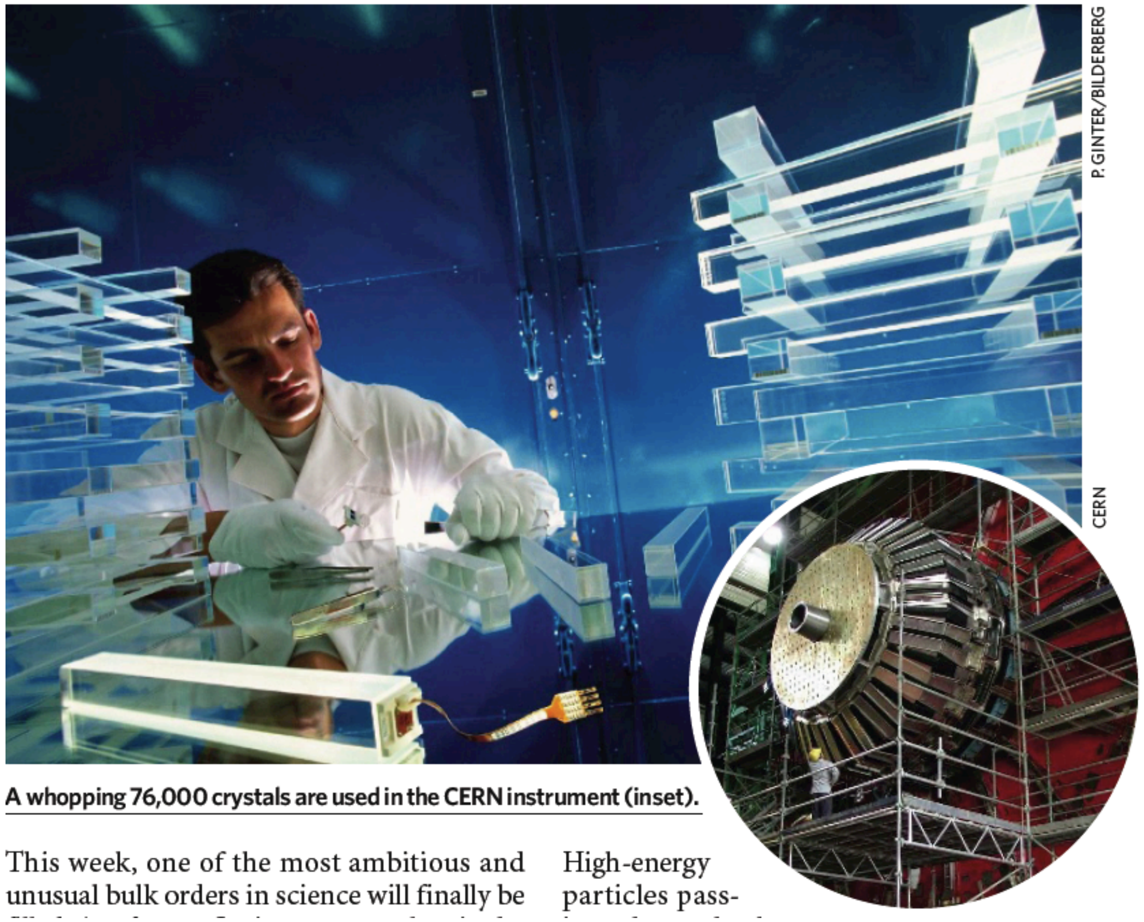
Technology

Crystal Growth is a Technology:



Estimated shares of world crystal production

Importance of single crystals



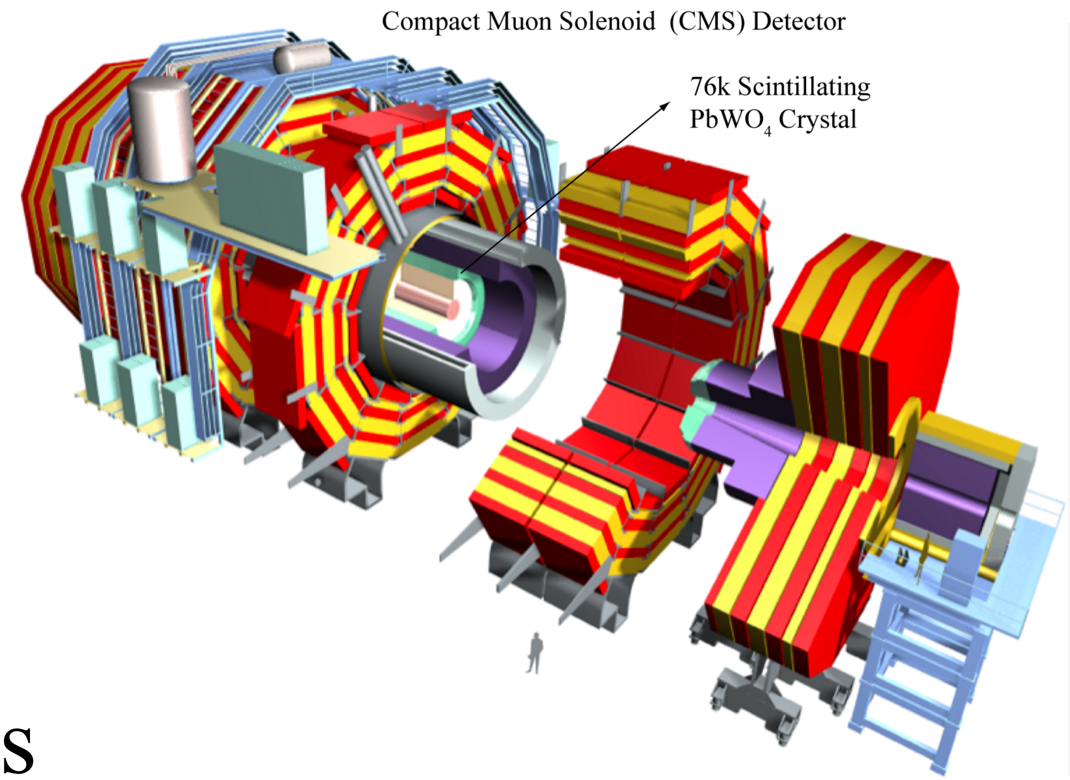
A whopping 76,000 crystals are used in the CERN instrument (inset).

This week, one of the most ambitious and unusual bulk orders in science will finally be

High-energy particles pass-

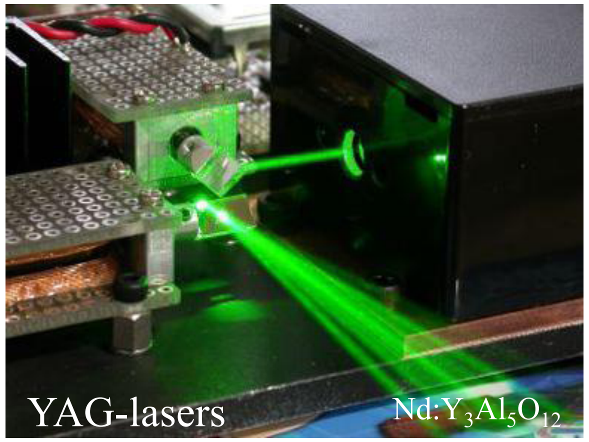
Large Hadron Collider

76,000 crystals of PbWO4 is used in the Compact Muon Solenoid (CMS) Detector.



Electronic devices

Lasers



Crystals that grow in our body

Calcium oxalate

Uric acid

Calcium phosphate

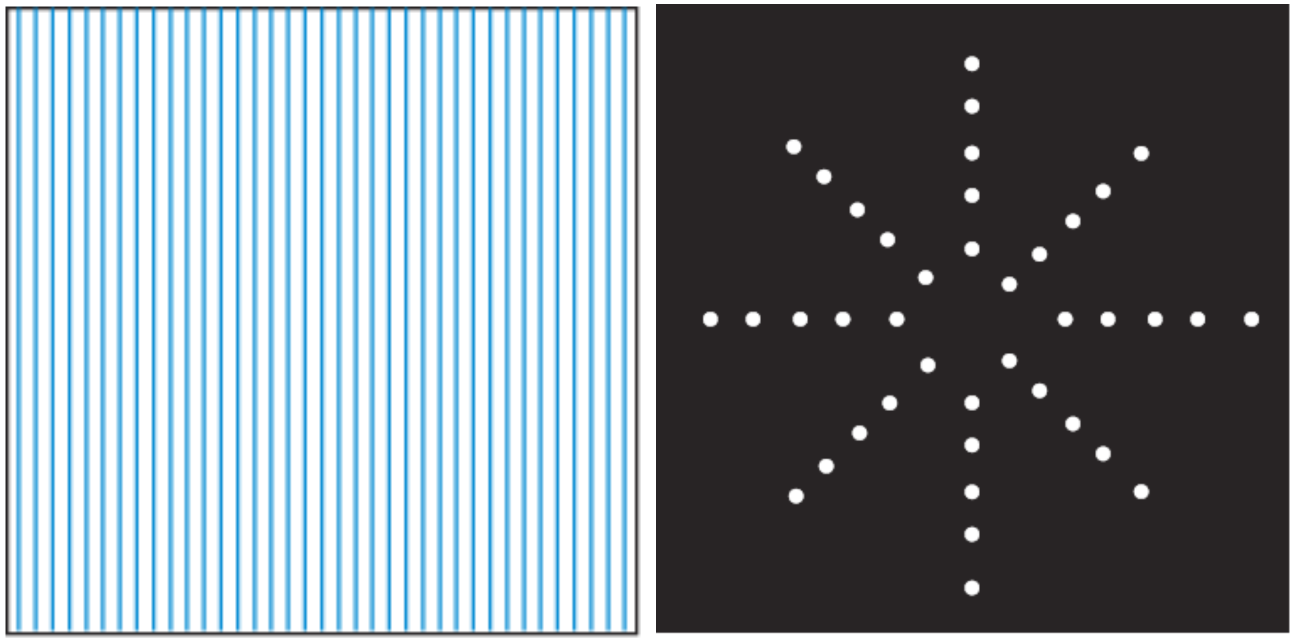
Single Crystal vs. Poly crystal

Single crystal: A homogenous body consisting of a three dimensional periodic arrangement of atoms, ions or molecules

Materials which produce diffraction spots are single crystalline

Poly crystal: A very large number of tiny crystallites

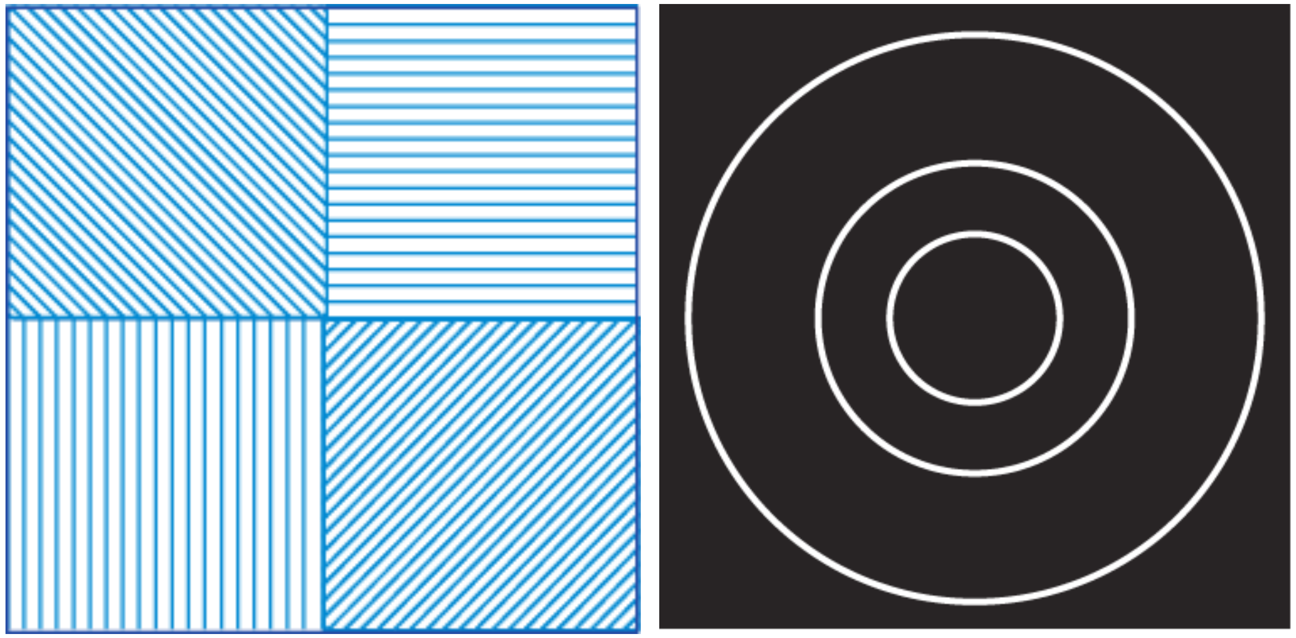
Single crystal:



No grain boundaries

Phase pure

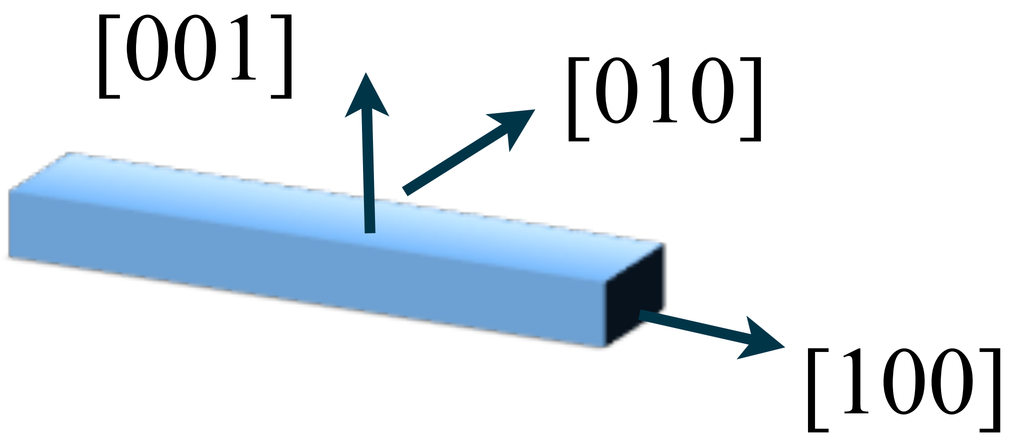
Poly crystal:



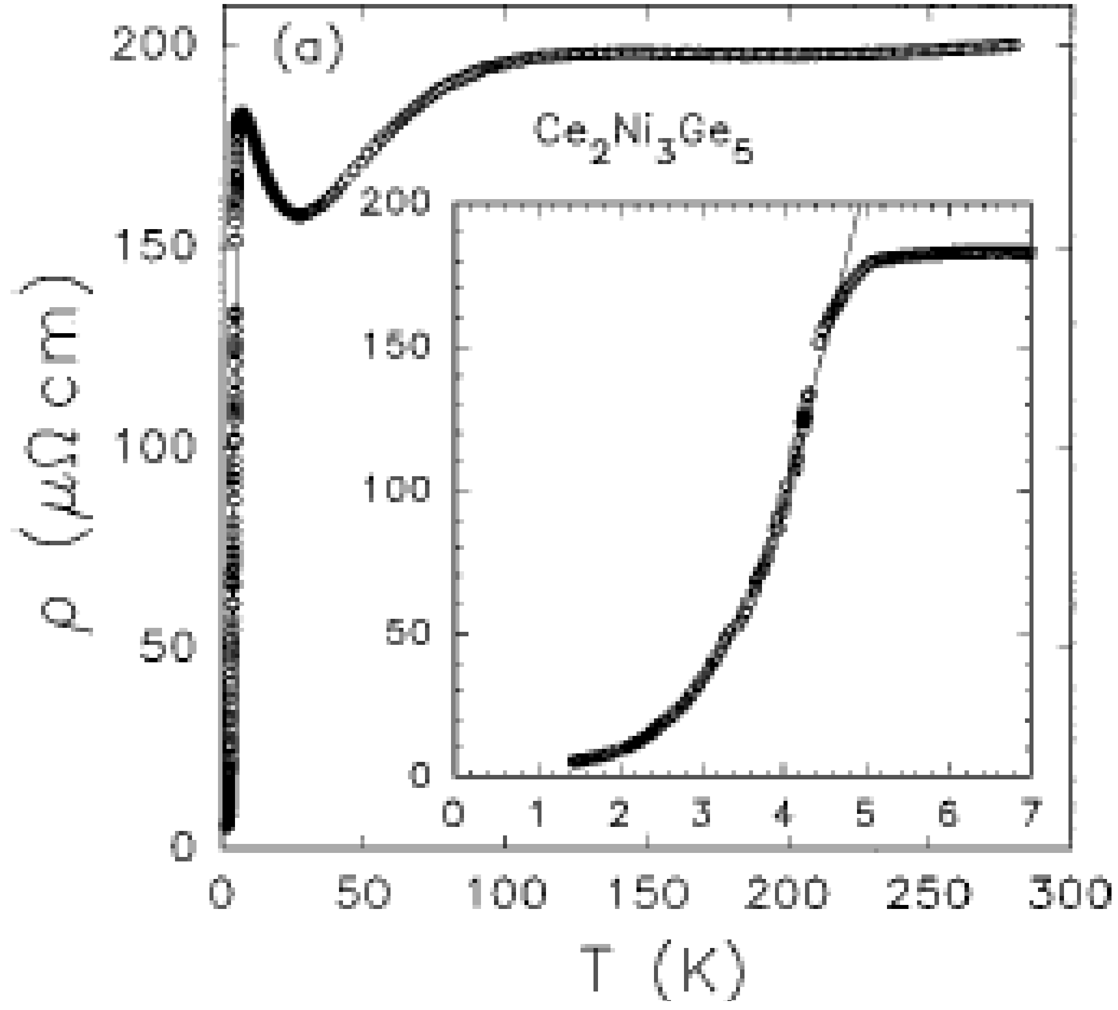
Grain boundaries

Multi-phase

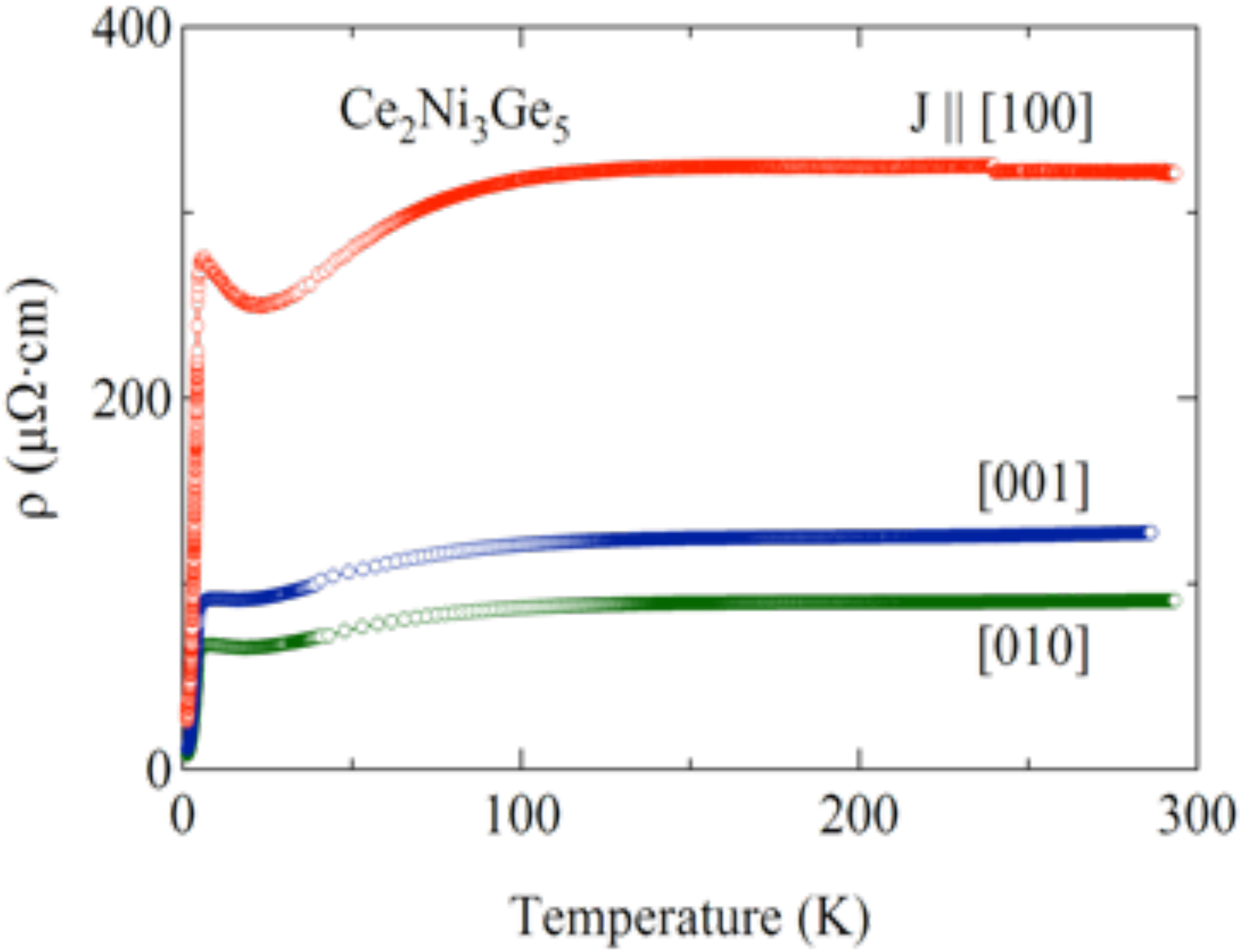
Electrical resistivity of $Ce_2Ni_3Ge_5$



Polycrystalline

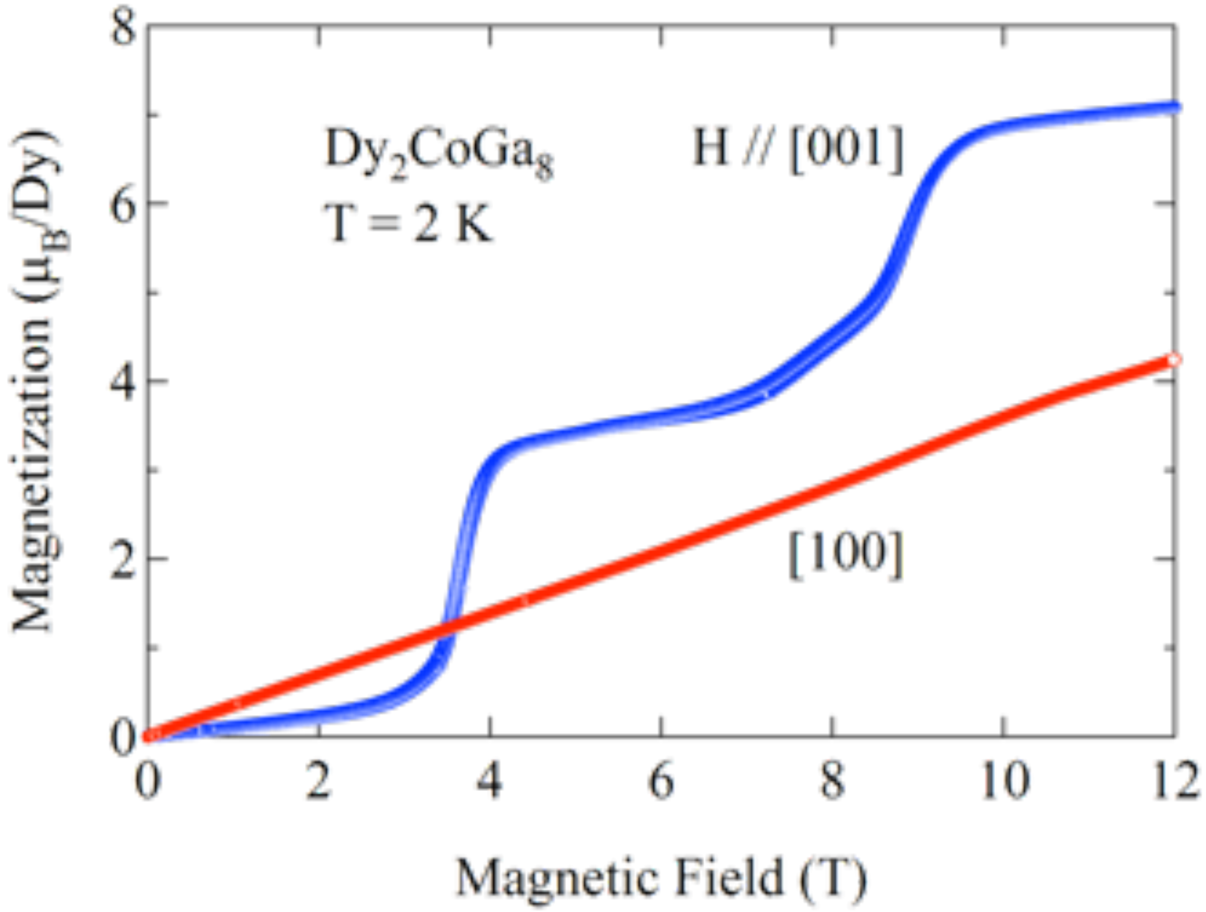


Average of three principal directions



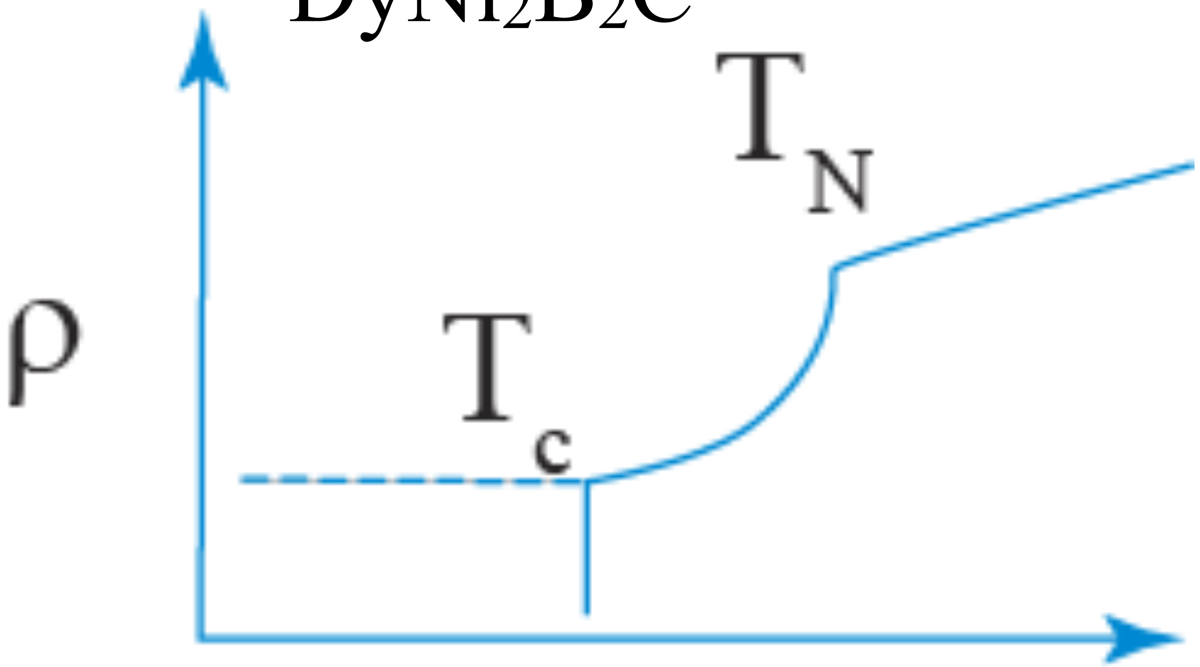
Large anisotropy reflecting the orthorhombic crystal structure

Some more examples



Anisotropy in magnetism
requires oriented single crystal

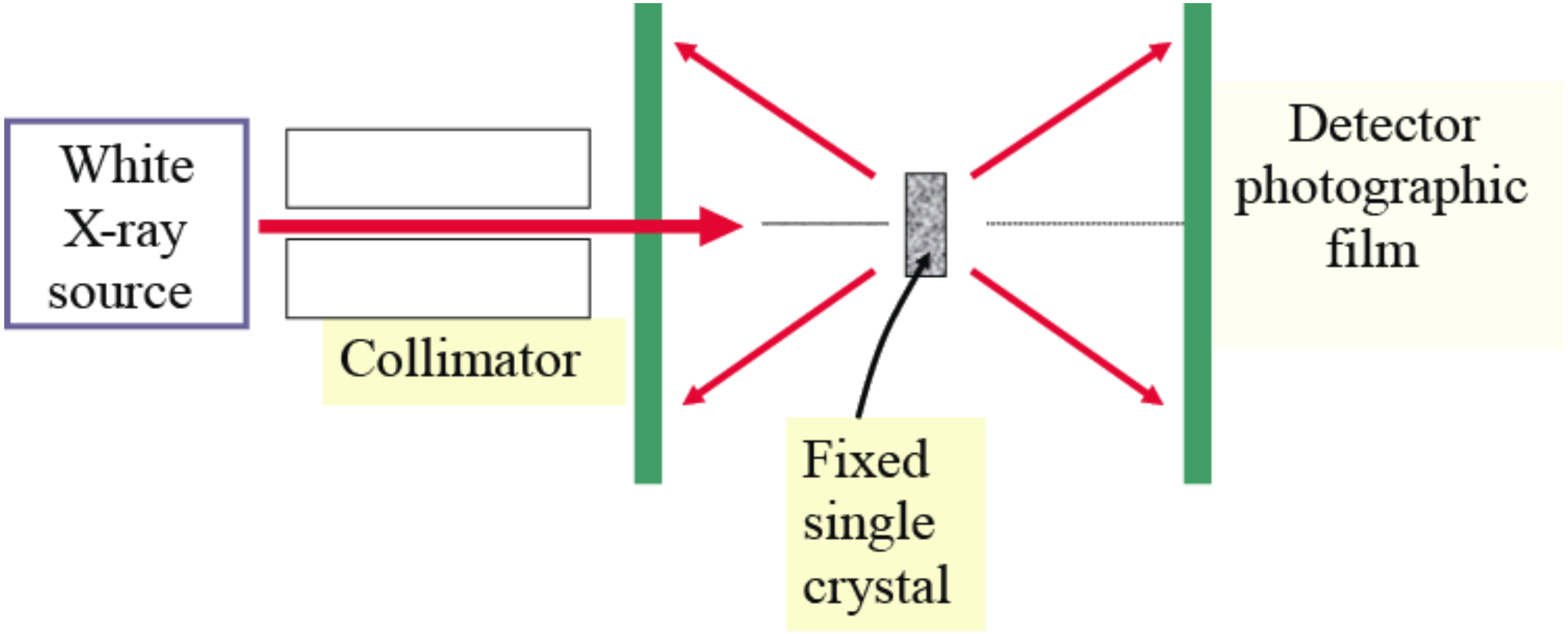
$DyNi_2B_2C$



Superconductivity - very sensitive to magnetic disorder / impurities

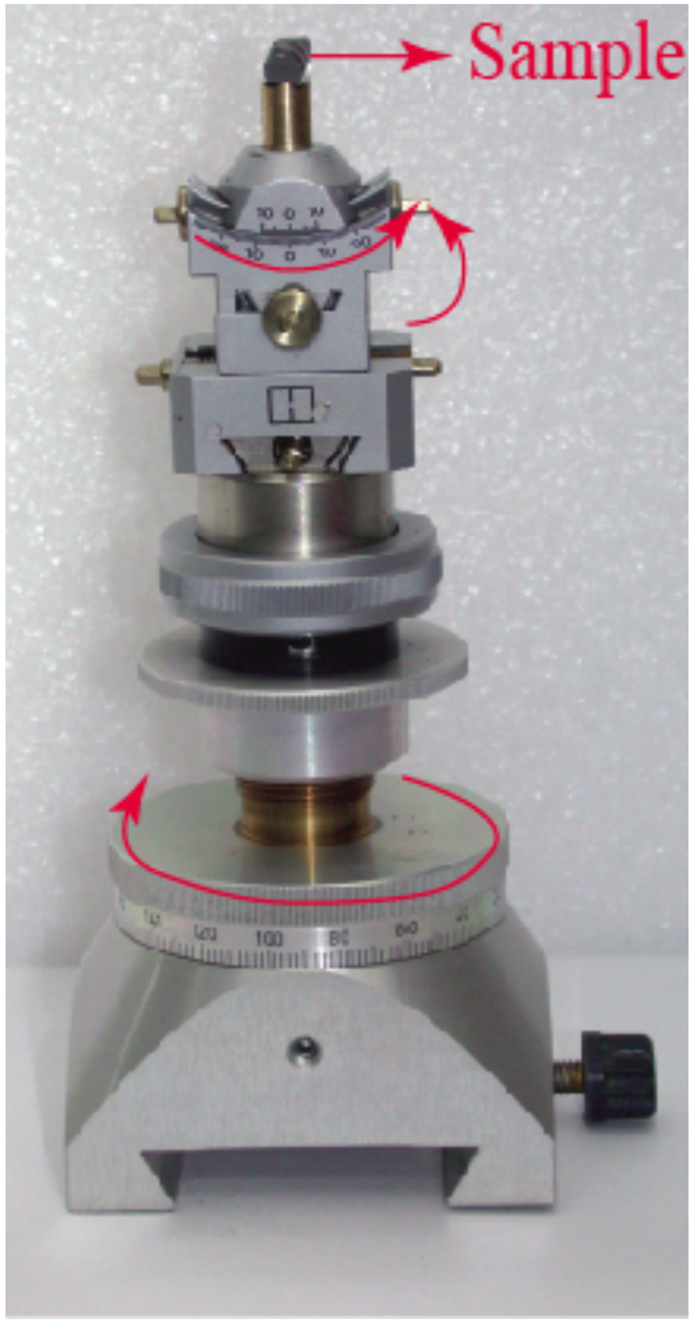
Orientation of the single crystal

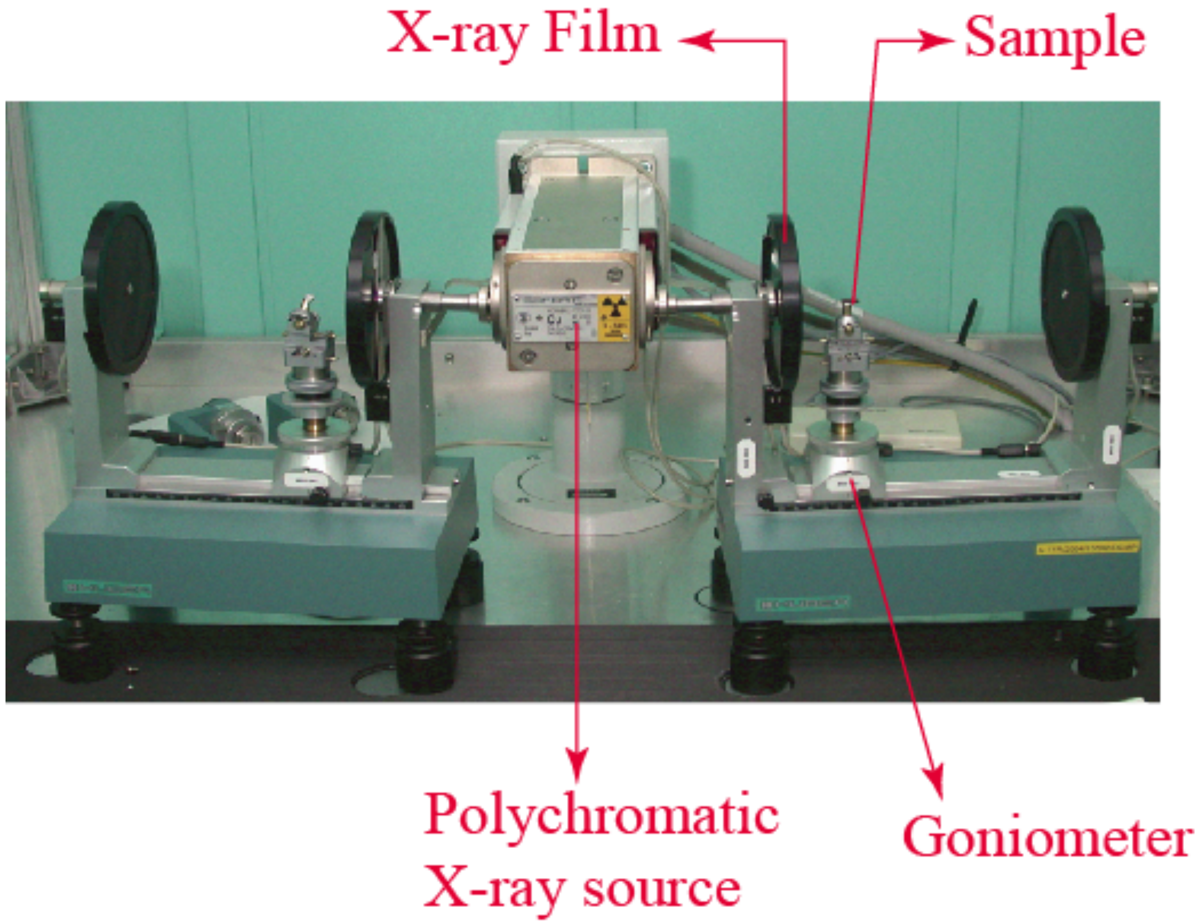
Laue method



θ is fixed λ is varying

Orientation and cutting





EDM cutting machine

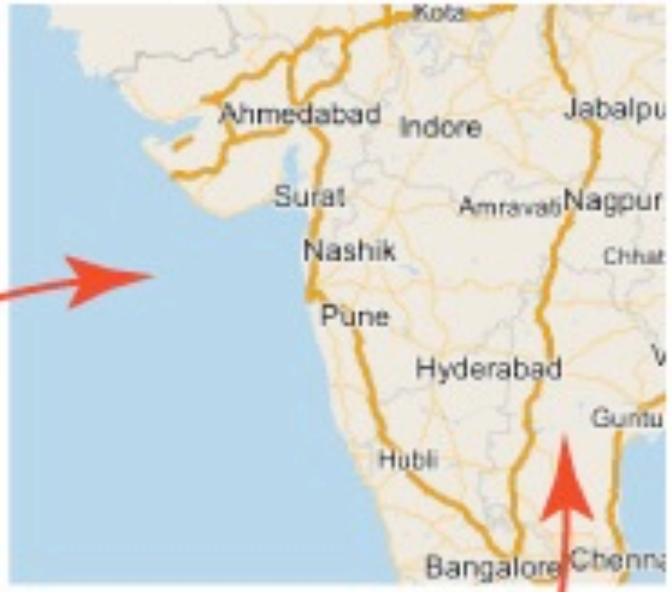
Crystal Growth

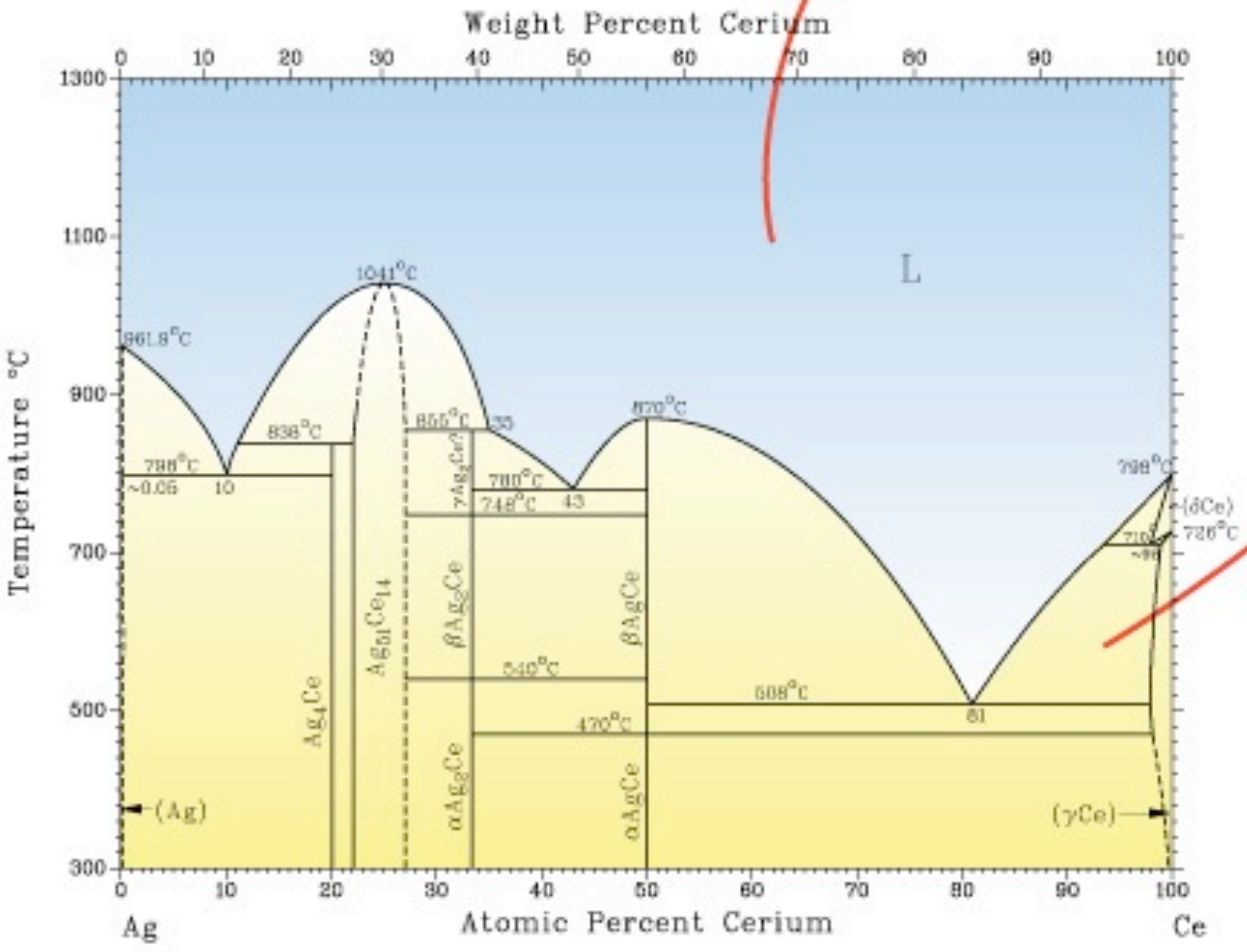
Crystals can be grown by variety of methods

- Low temperature solution growth
- Melt growth
  - Bridgman method
  - Czochralski method
  - High temperature solution growth
- Vapour growth
  - Physical vapour transport
  - Chemical vapour transport

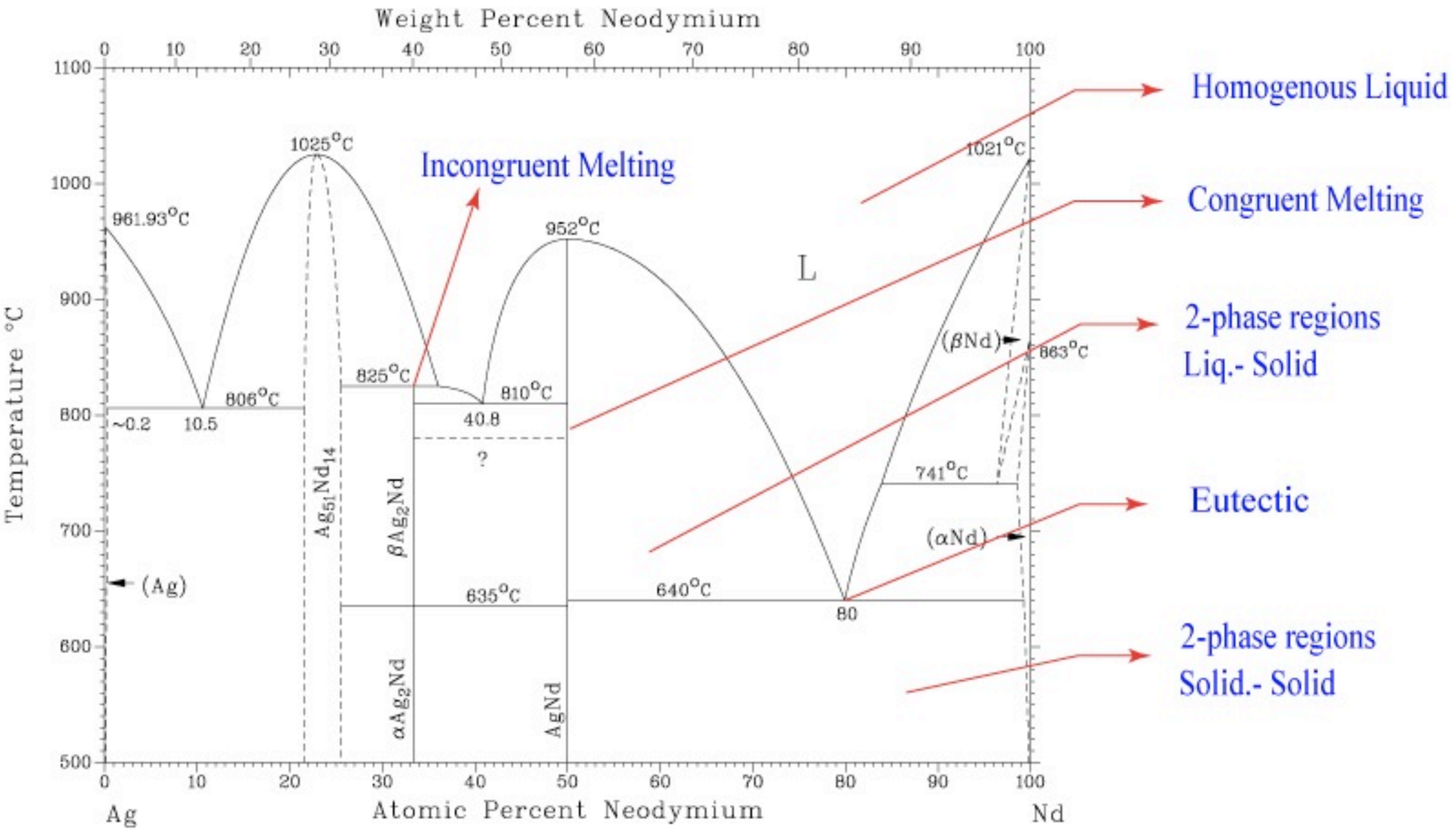
Phase diagram - recap

Binary phase diagrams can be simply thought of as maps. They show the regions of liquid and solid





Binary phase diagram of Ag-Nd



Incongruent Melting

Homogenous Liquid

Congruent Melting

2-phase regions

Liq.- Solid

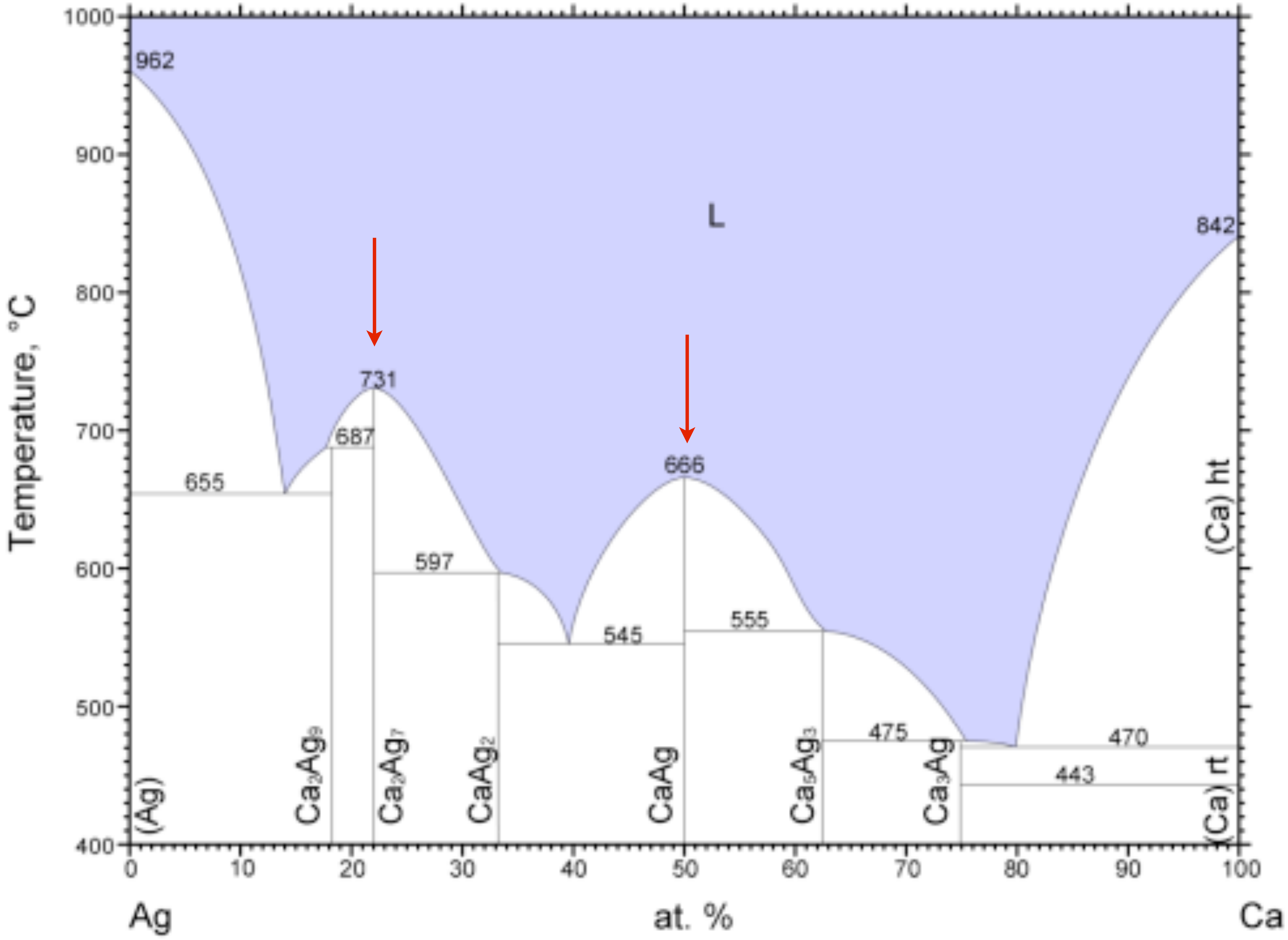
Eutectic

2-phase regions

Solid.- Solid

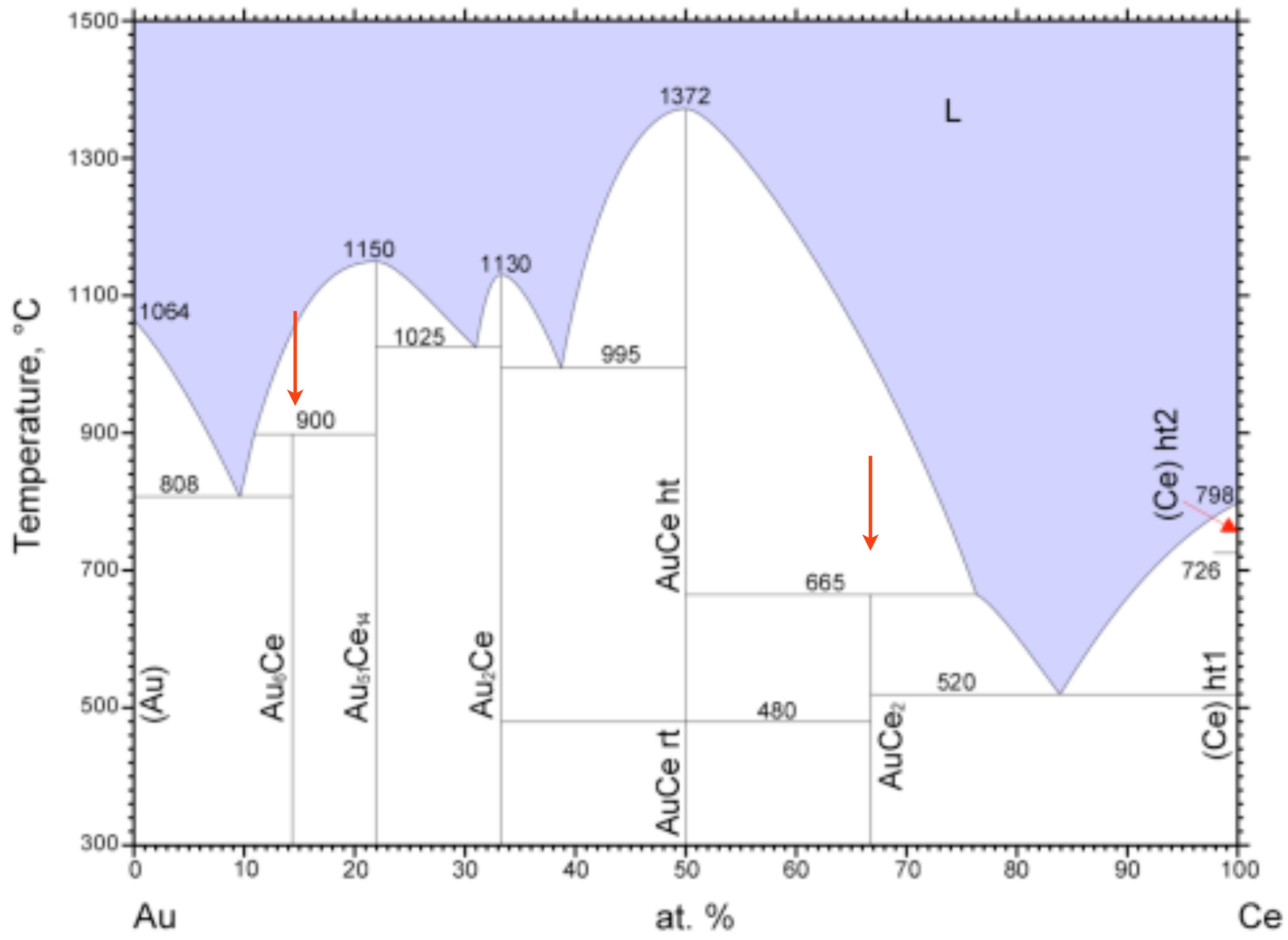
Congruent melting

Transforms from a homogenous liquid to homogenous solid



Peritectic reaction

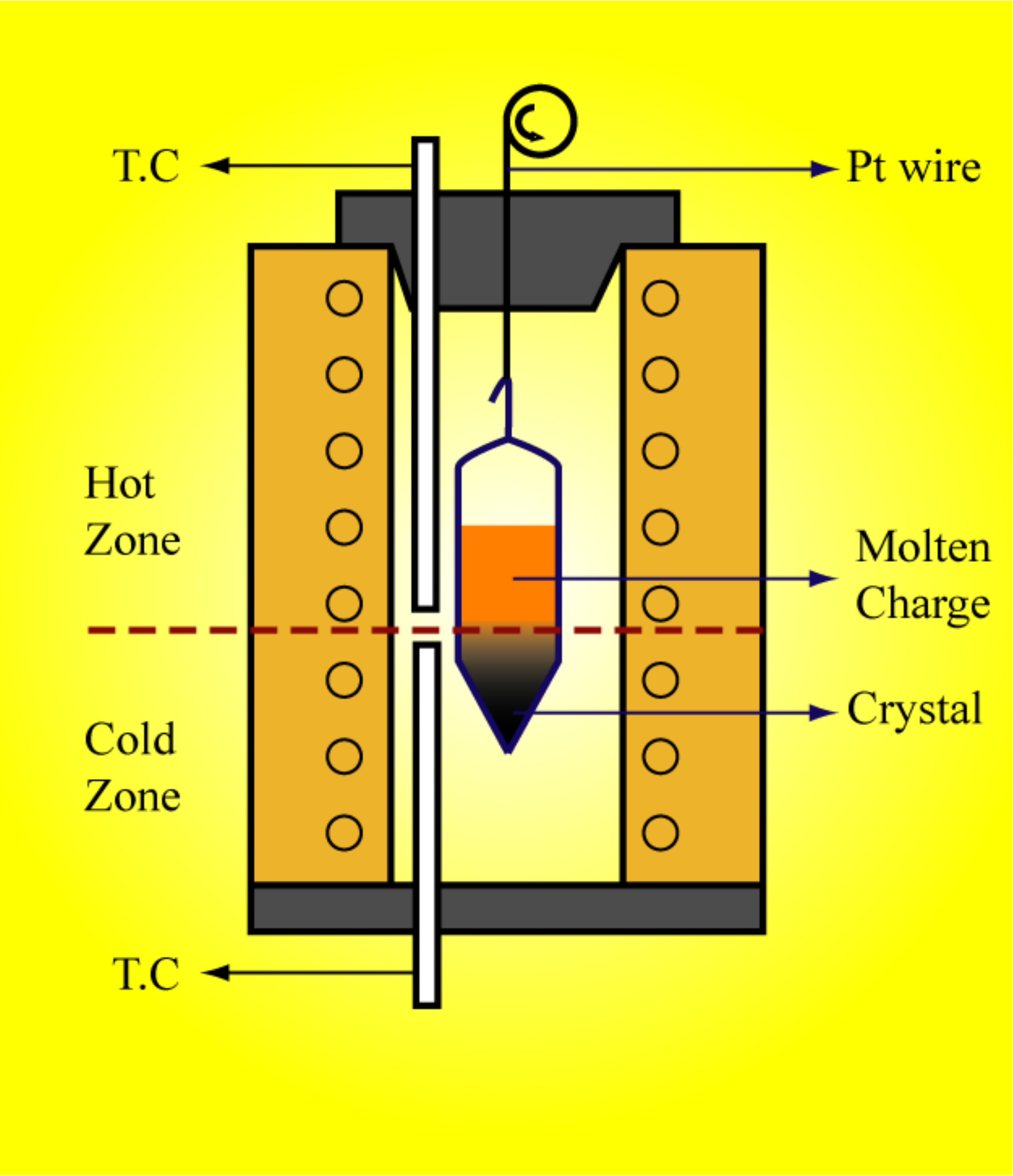
Decompose into a mixed solid and a liquid phase (Incongruent metling)



Crystal growth methods

Bridgman method

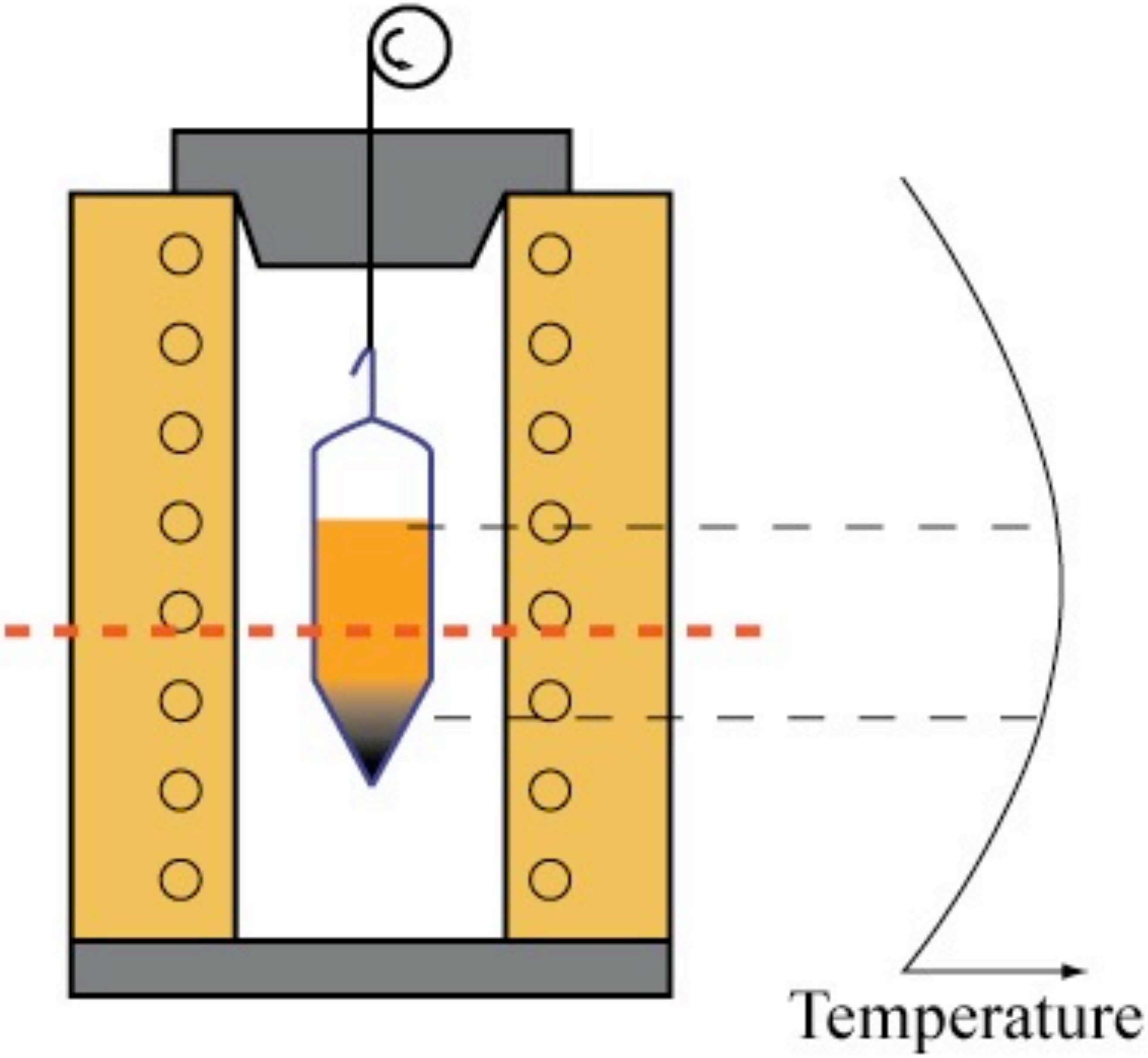
Samples that melt congruently, but have high vapour pressure



The ampoule is lowered slowly from hot zone to cold Zone (maintained below the melting point)

Bridgman method

Temperature gradient method - Static Freeze method

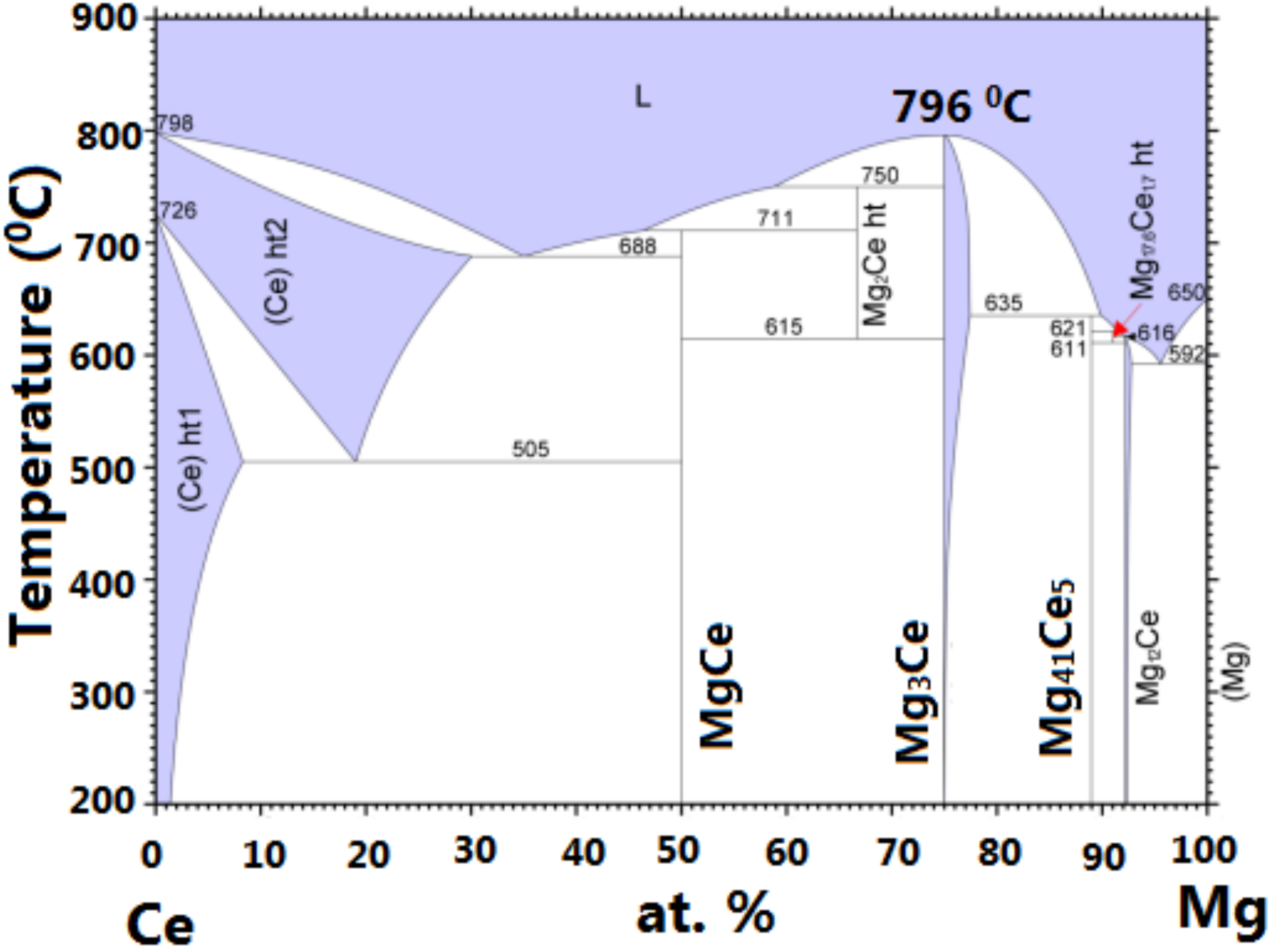


Typical temperature
gradient 10 to 30 °C

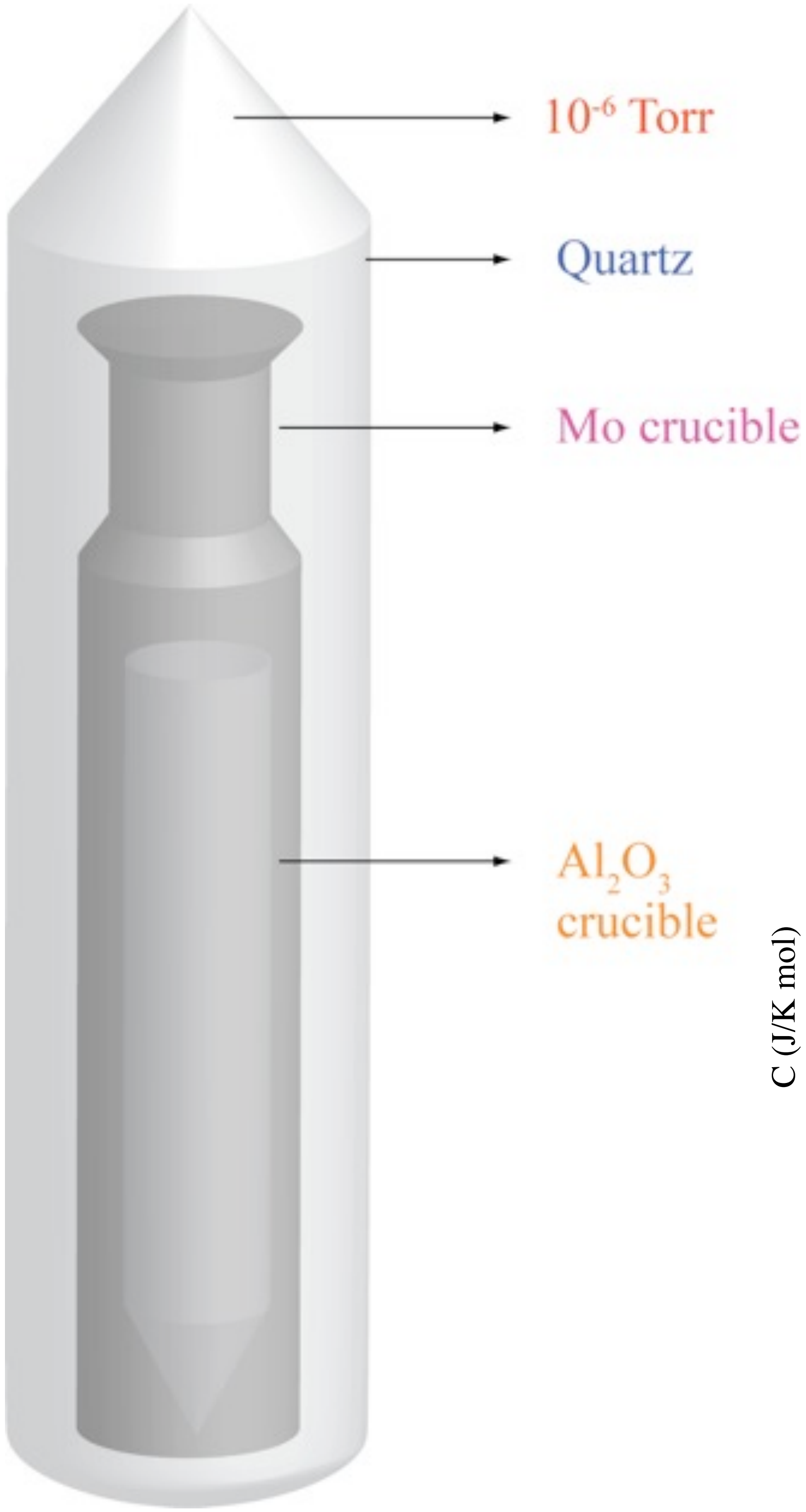
Crystal growth of $CeMg_3$

$CeMg_3$ melts congruently

Mg has high vapor pressure



$CeMg_3$ continued...



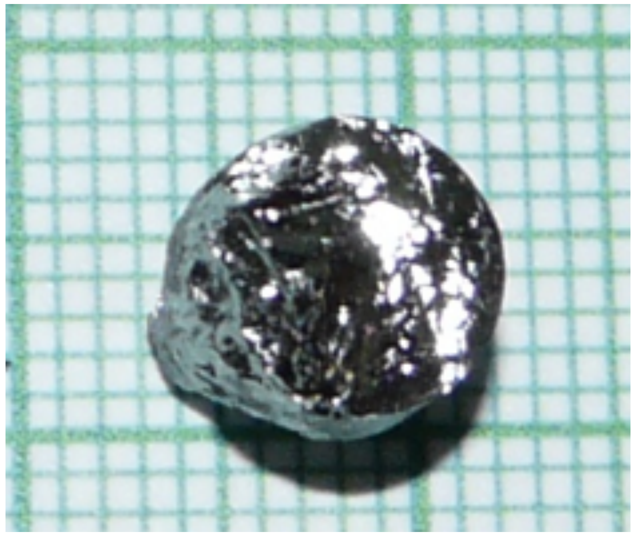
10^{-6} Torr

Quartz

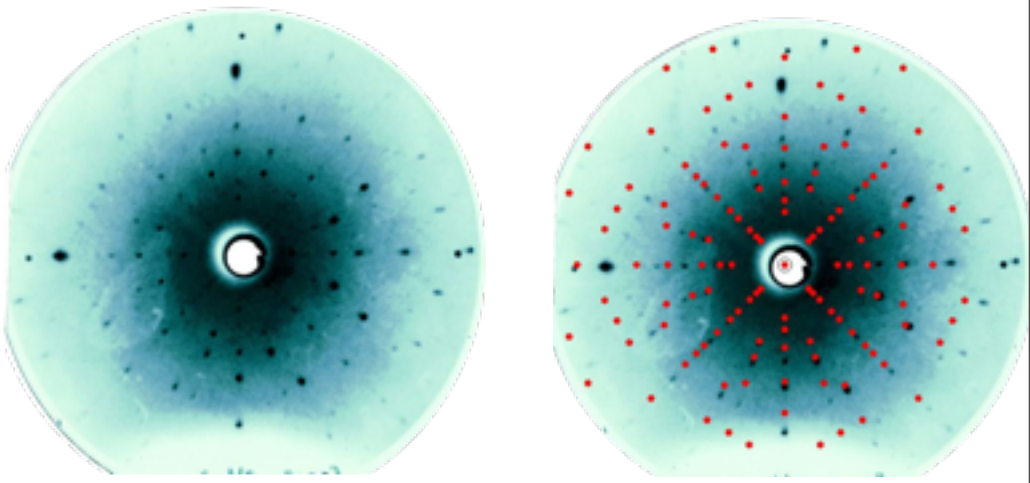
Mo crucible

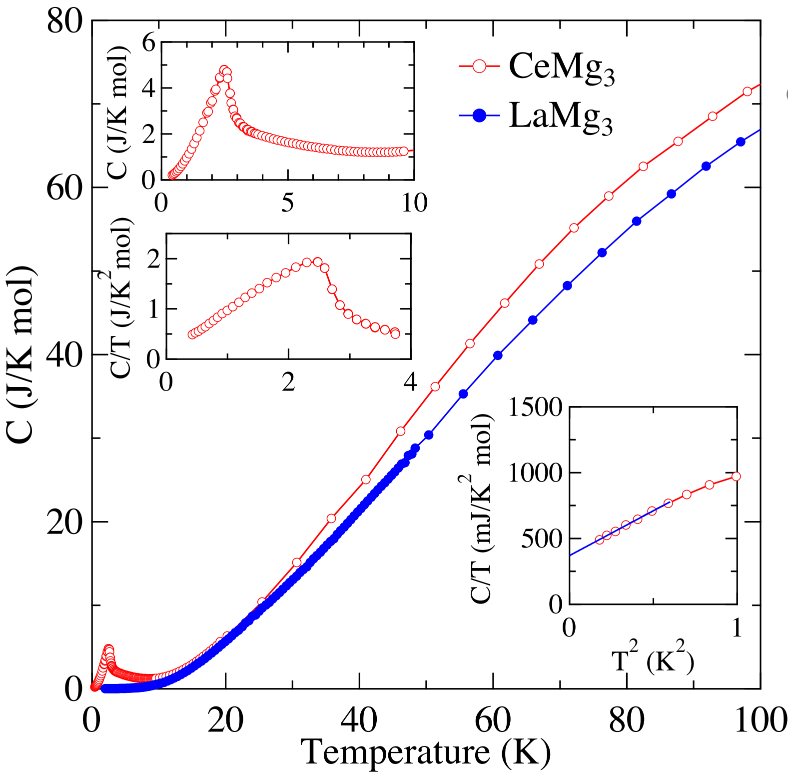
Al_2O_3 crucible

As grown crystal

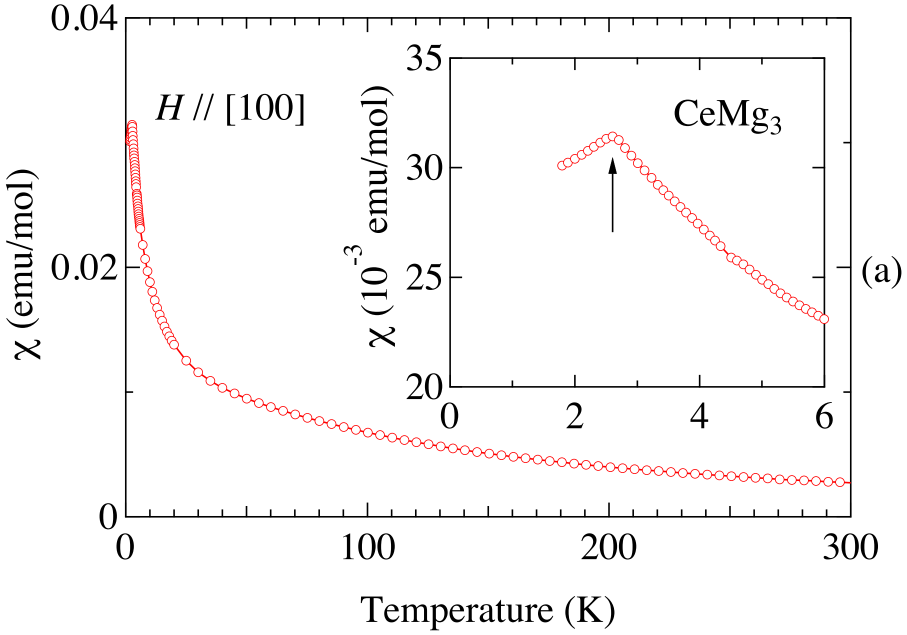


Laue Pattern (100)





γ = 370 mJ/K^2 mol



Pranab Kumar Das et al.,
To be published in Phys. Rev. B April 2011

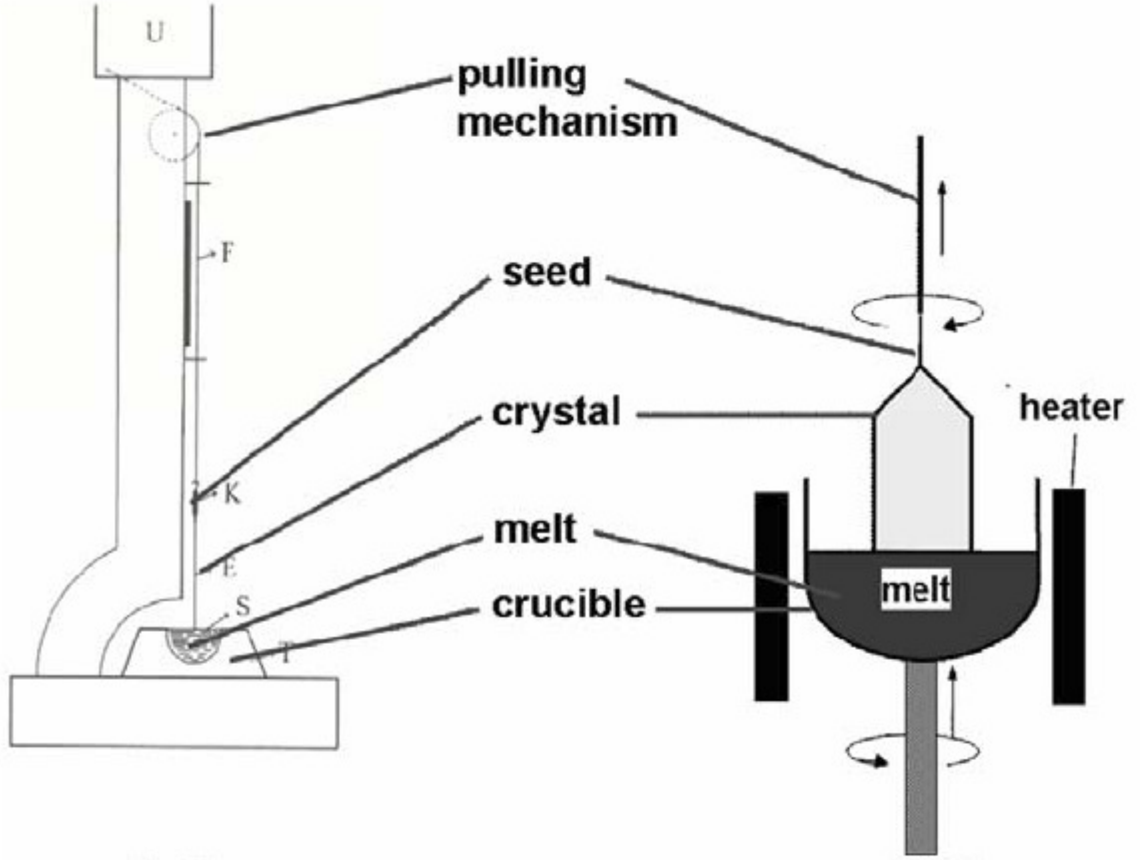
Czochralski method

Prof. Jan Czochralski
Poland
(1885 - 1953)
Solidification of metals

Materials that melt congruently can be grown by this method

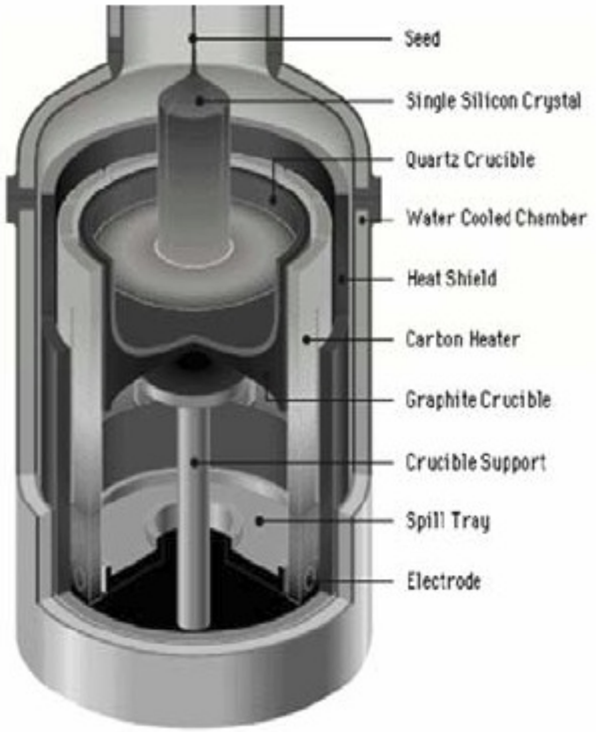
About 90 years ago

Si single crystal



1917

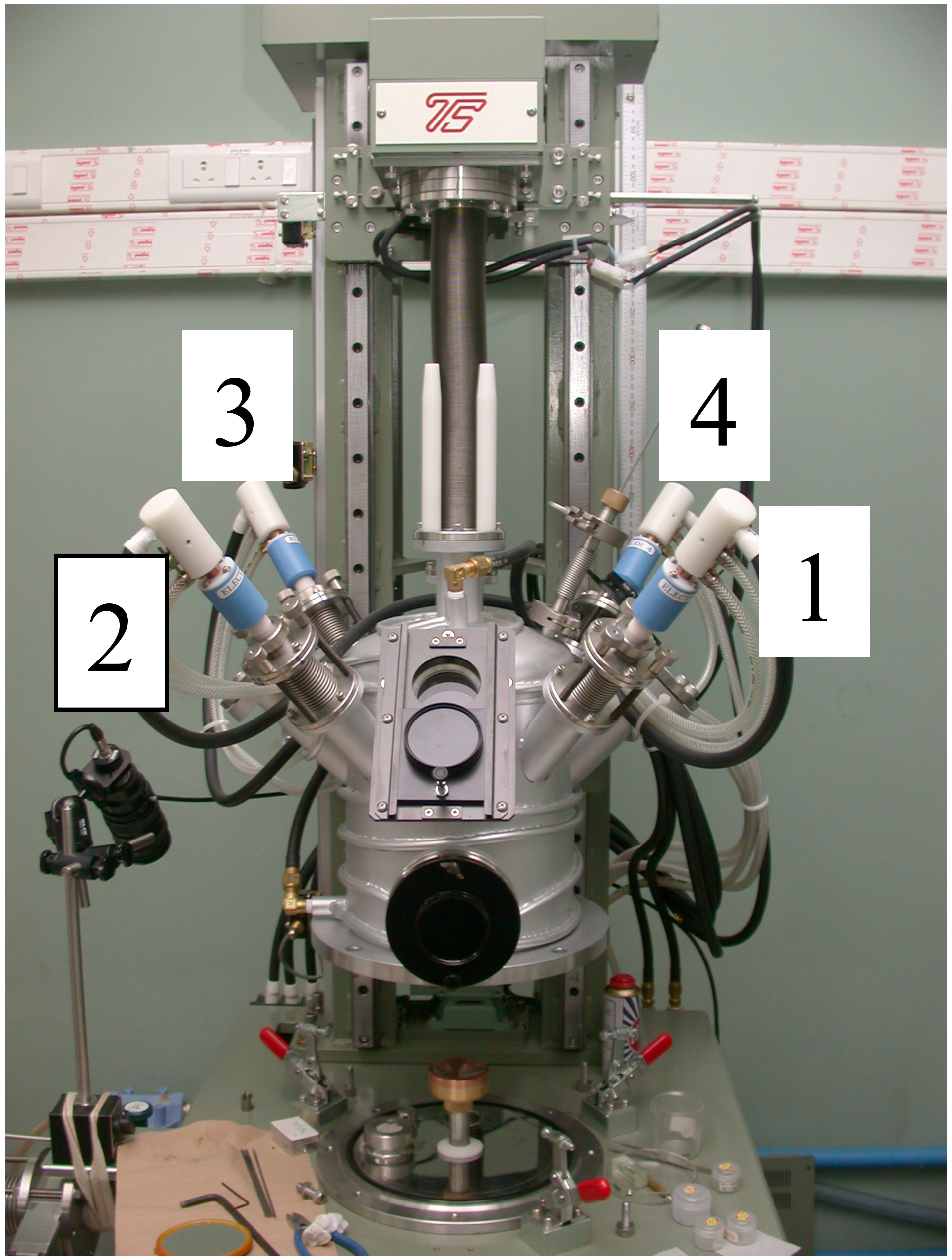
1950

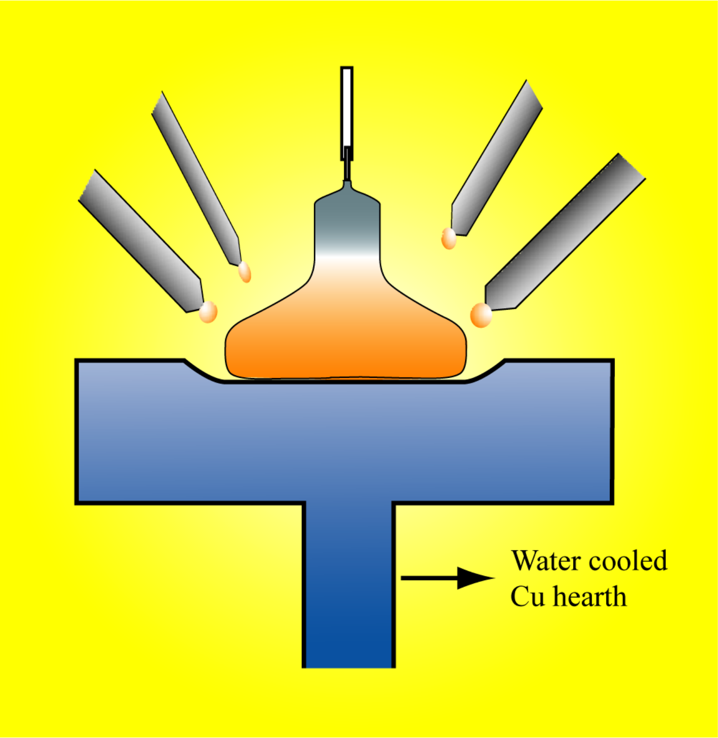


today

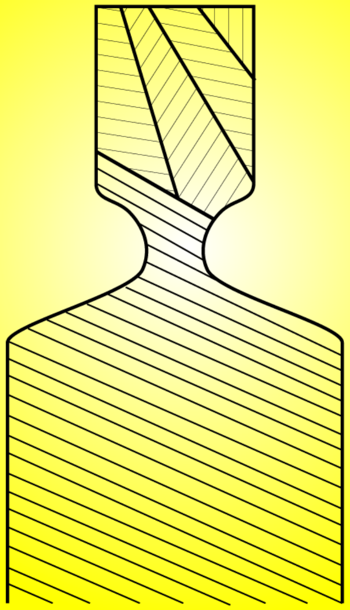
200 kg

Czochralski method for rare-earth intermetallics

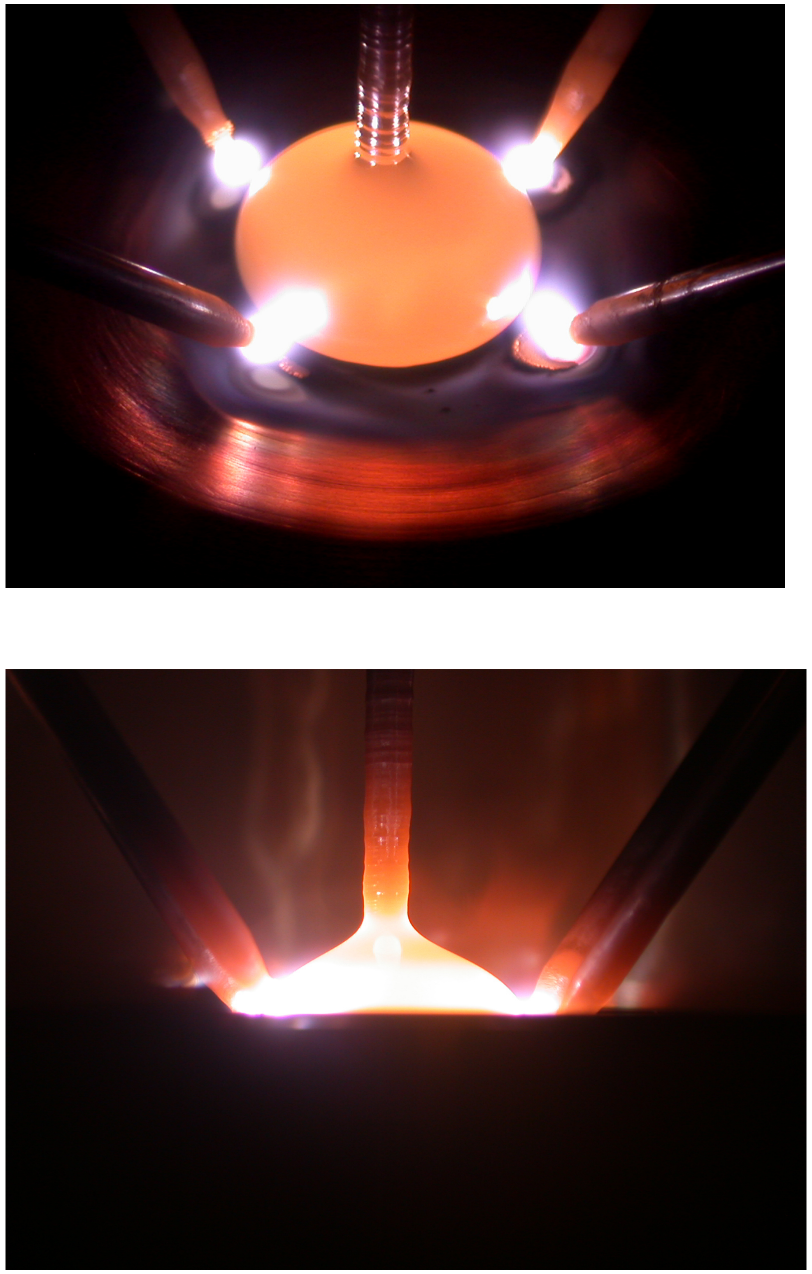




Necking, to select a single crystal seed



During crystal growth

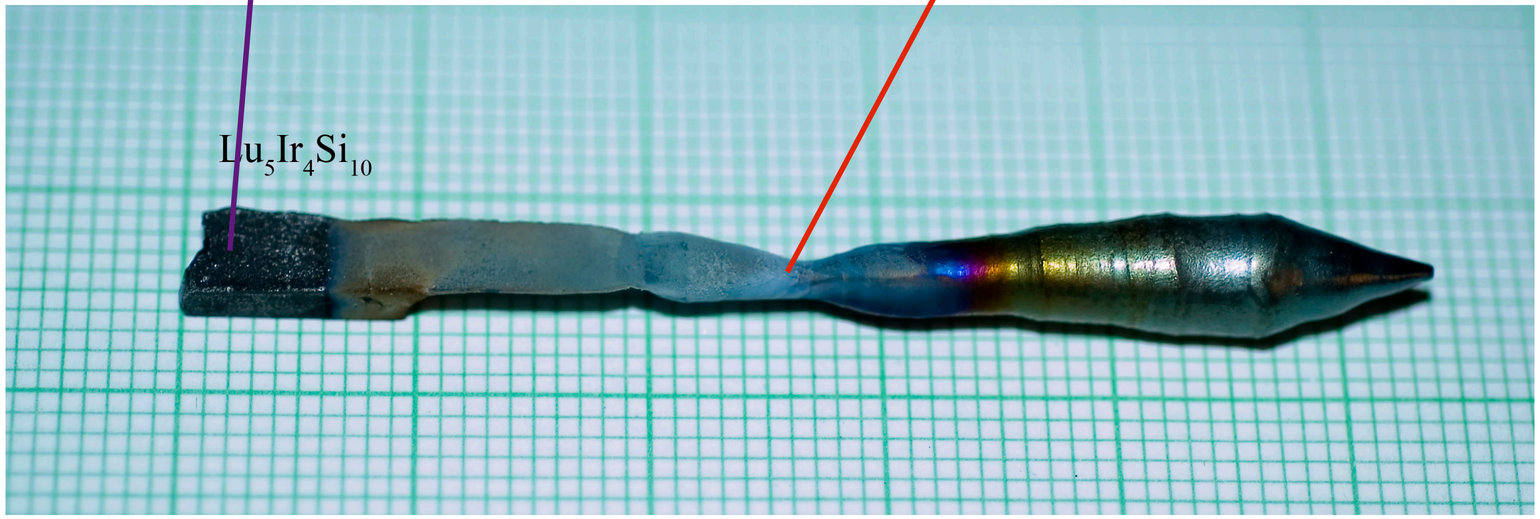


Crystal pulling 10 - 15 mm/hr

Czochralski growth of $Lu_5Ir_4Si_{10}$

Polycrystalline seed

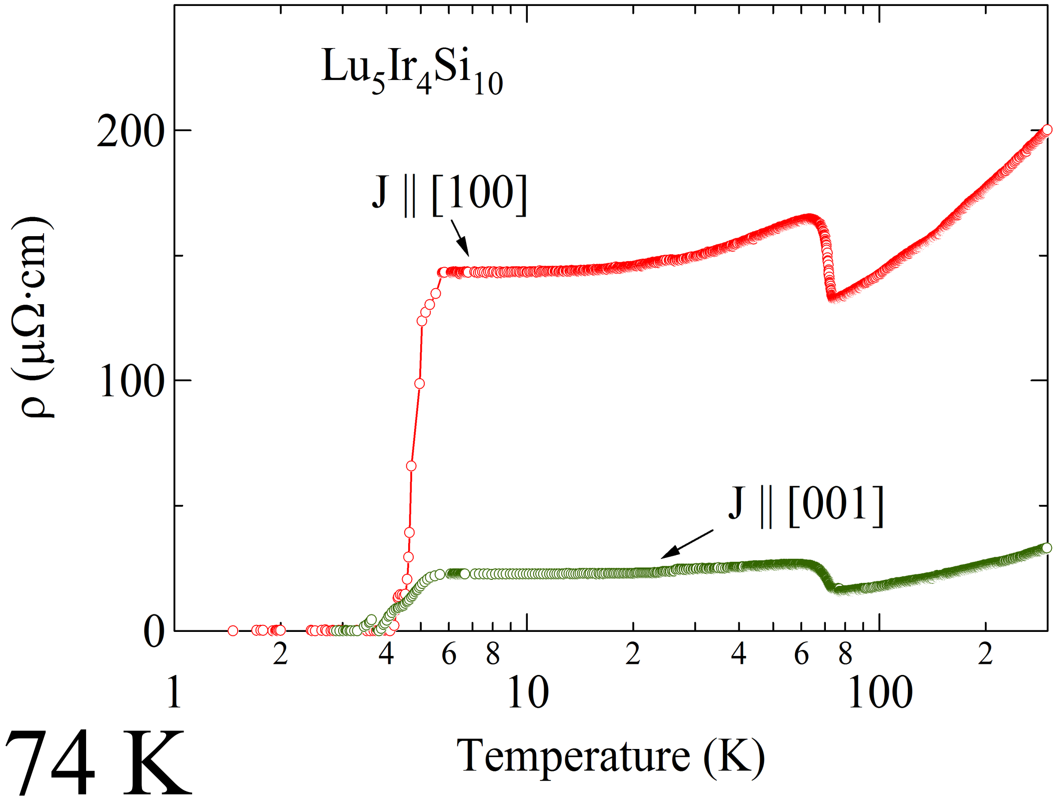
Necking



Tetragonal crystal structure

$$a = 12.494\ \text{Å}$$

$$c = 4.185\ \text{Å}$$



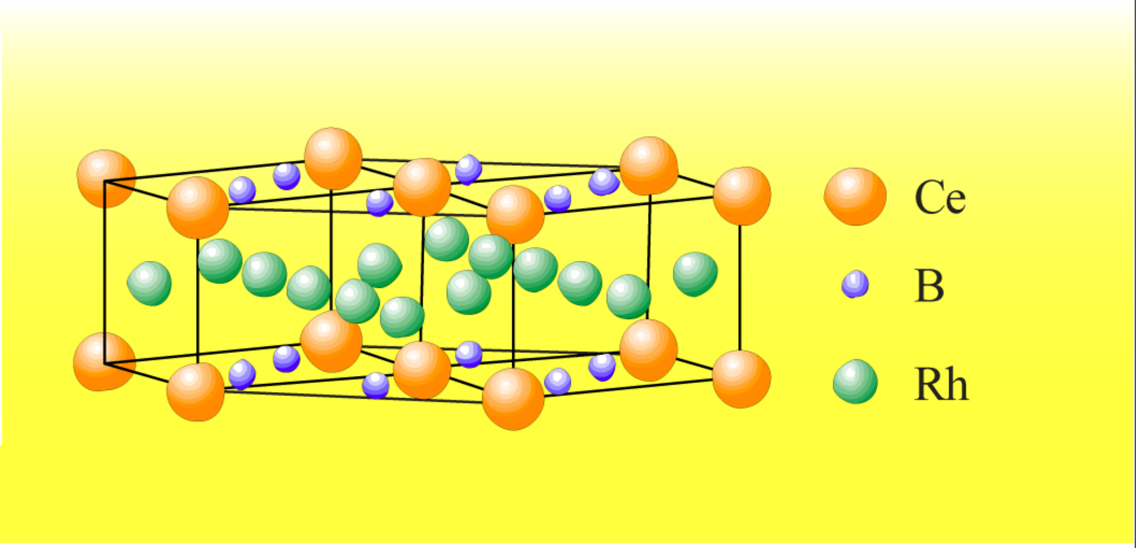
$T_c = 5.7$ K and $T_{CDW} = 74$ K

Czochralski growth of $CeRh_3B_2$

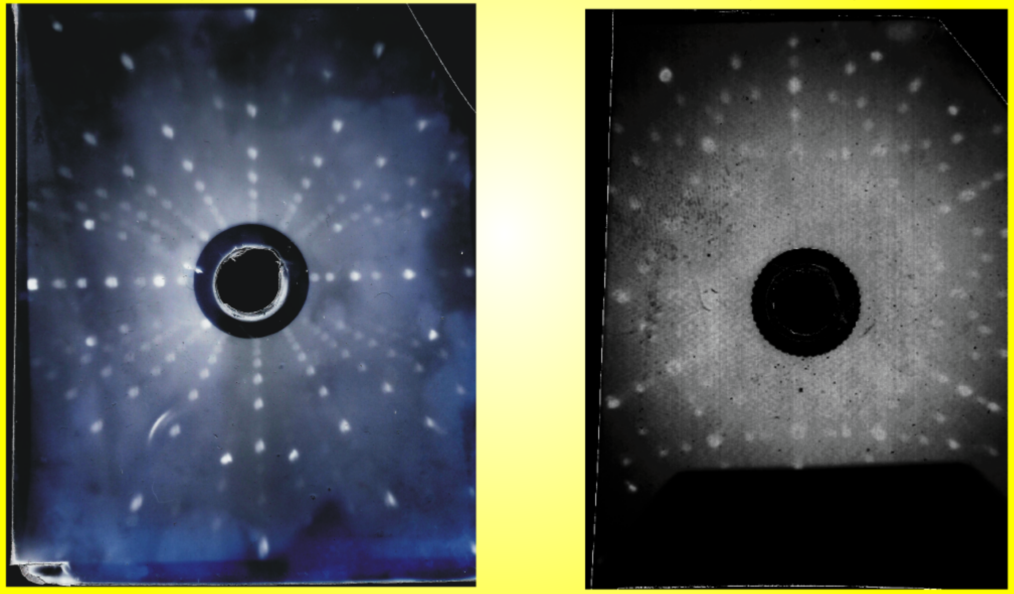
Strong itinerant magnetism in ternary boride $CeRh_3B_2$

S K Dhar, S K Malik and R Vijayaraghavan
Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400005, India

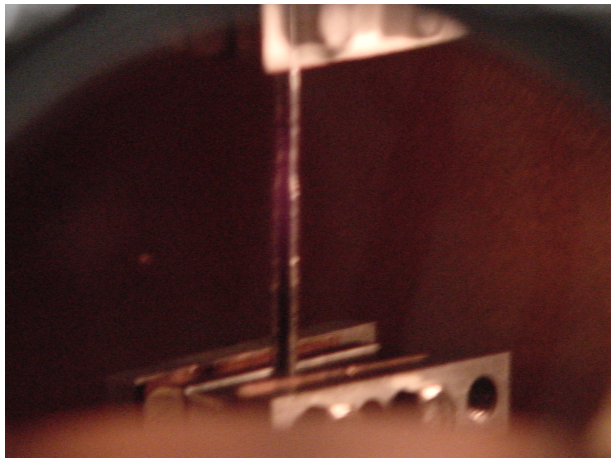
Received 5 February 1981



Laue Pattern of $CeRh_3B_2$ single crystal


$(10\bar{1}0)$ (0001)

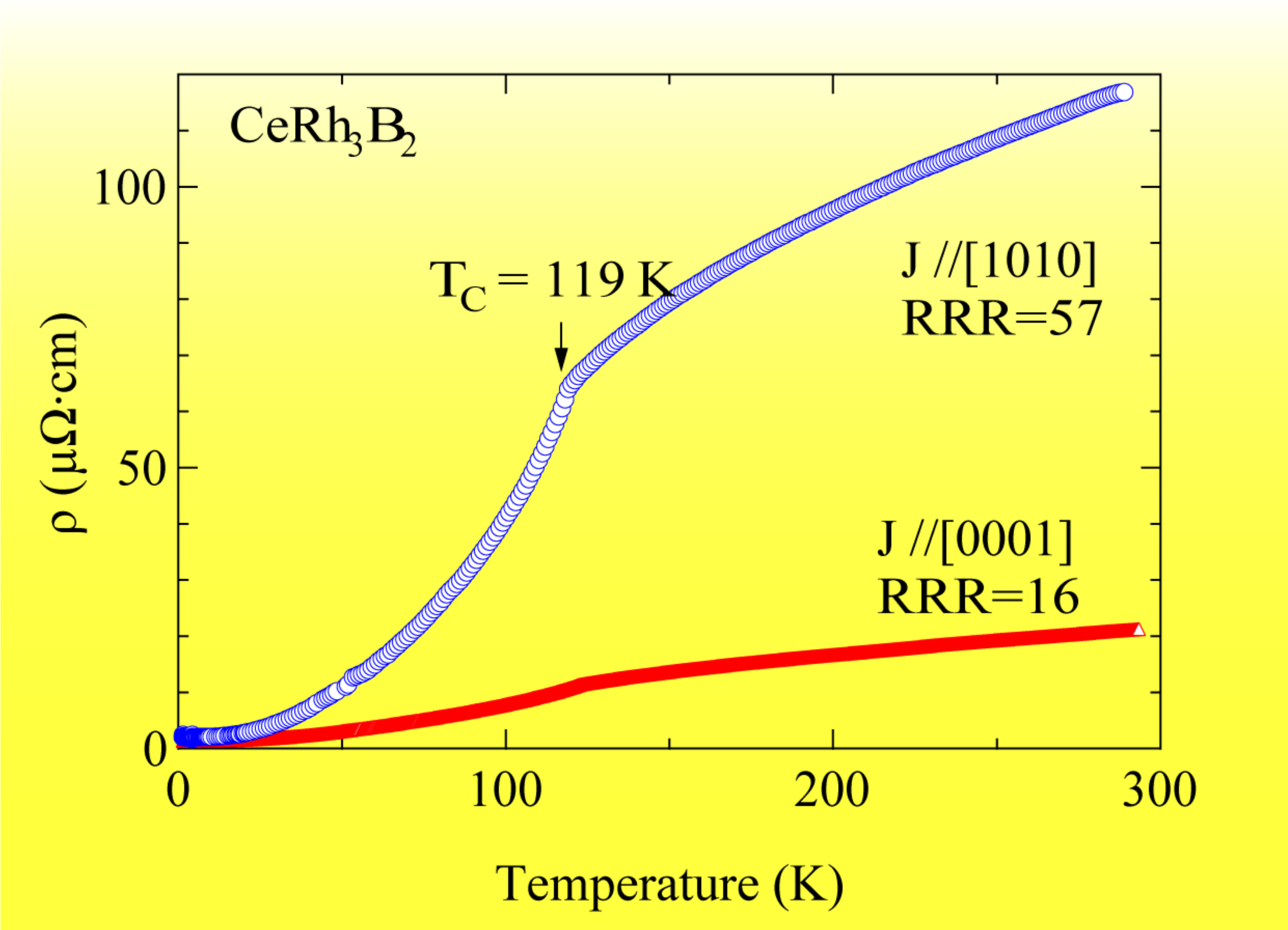
As grown single crystal



Solid state electrotransport

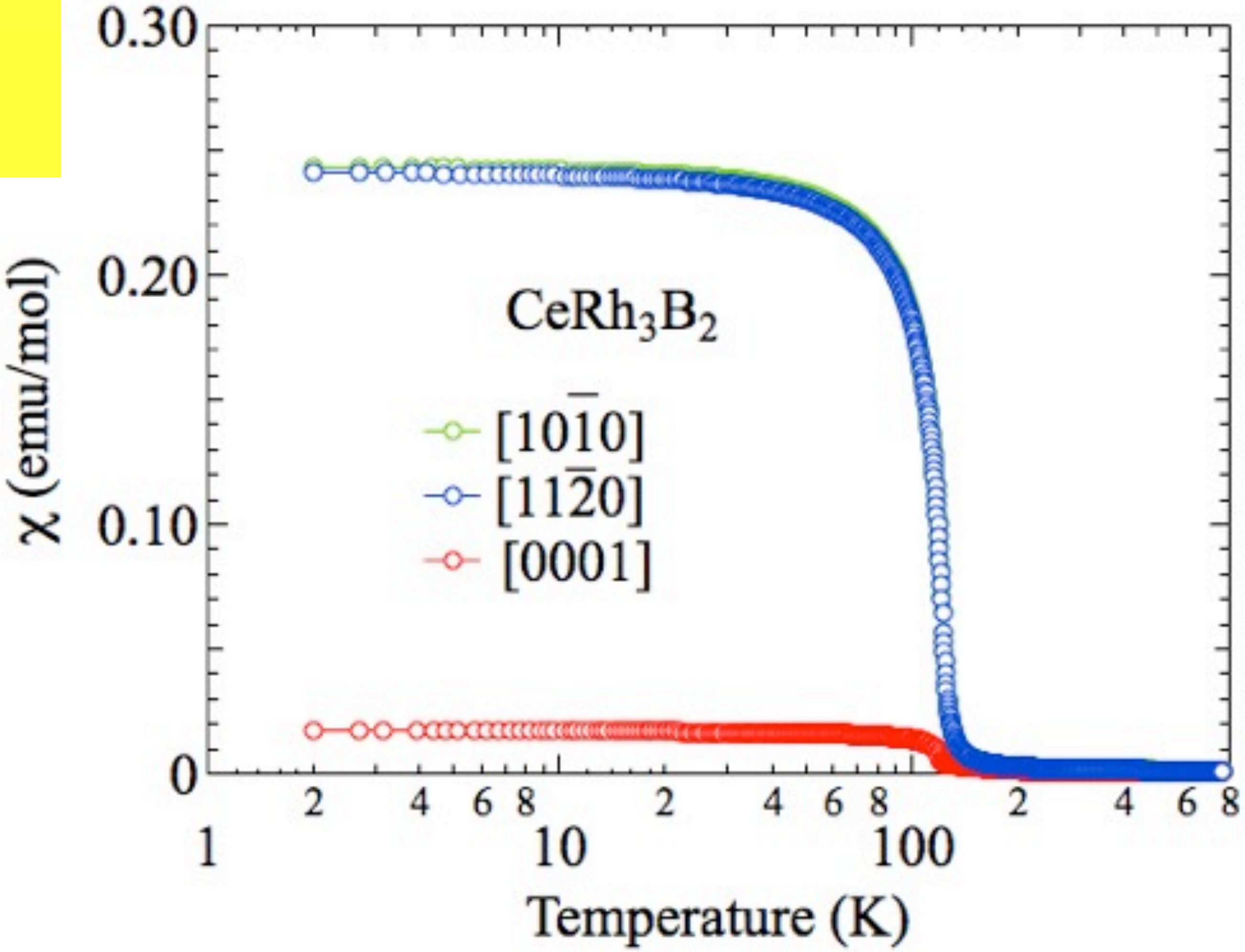
10^{-9} Torr 40 A current

Anisotropic magnetic properties of $CeRh_3B_2$



Electrical resistivity

Mag. Susceptibility

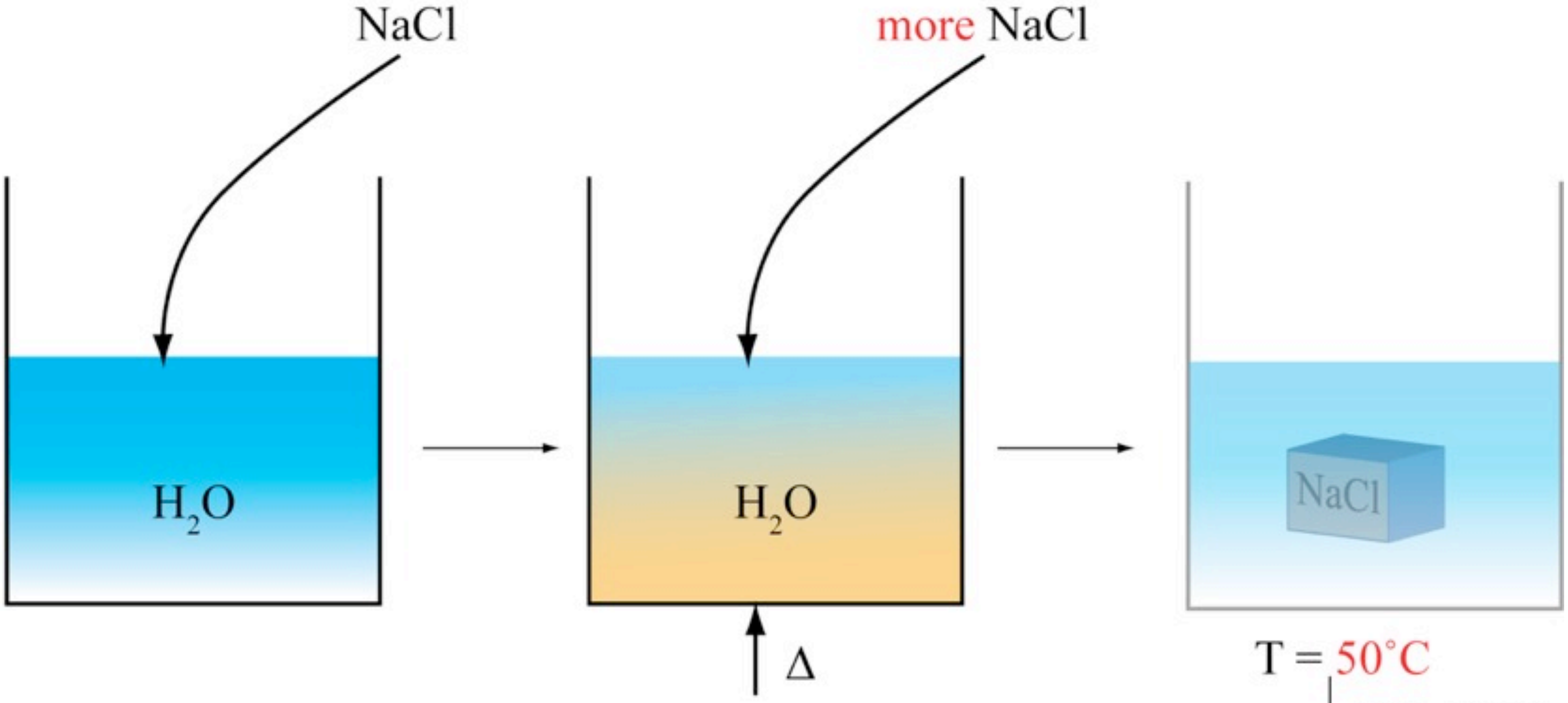


Crystal growth from High Temperature Solution

(Flux growth)

Crystal growth from High Temperature Solution
(Flux growth)

Low Temperature Solution Growth:



At T = 30°C (R.T)

NaCl completely dissolves

Add more NaCl to make a saturated solution

At T = 50°C

We can add ,more NaCl and the solution becomes Supersaturated solution

T = 50°C

@ 0.01°C

T = 30°C

Well FACTED single crystal

Crystal growth from High Temperature Solution
(Flux growth)

Crystal growth is done at high temperature

Incongruently melting compounds can be grown

Materials that have high vapour pressure

The growing crystal is NOT exposed to steep temperature gradient – the crystal grows free from mechanical and thermal constraints into the solution and so develop FACETS.

Since the crystal growth process is at elevated temperatures, one has to take care about the crucible (container material) and the choice of the flux

Choice of the crucible: Al_2O_3

Choice of solvents:

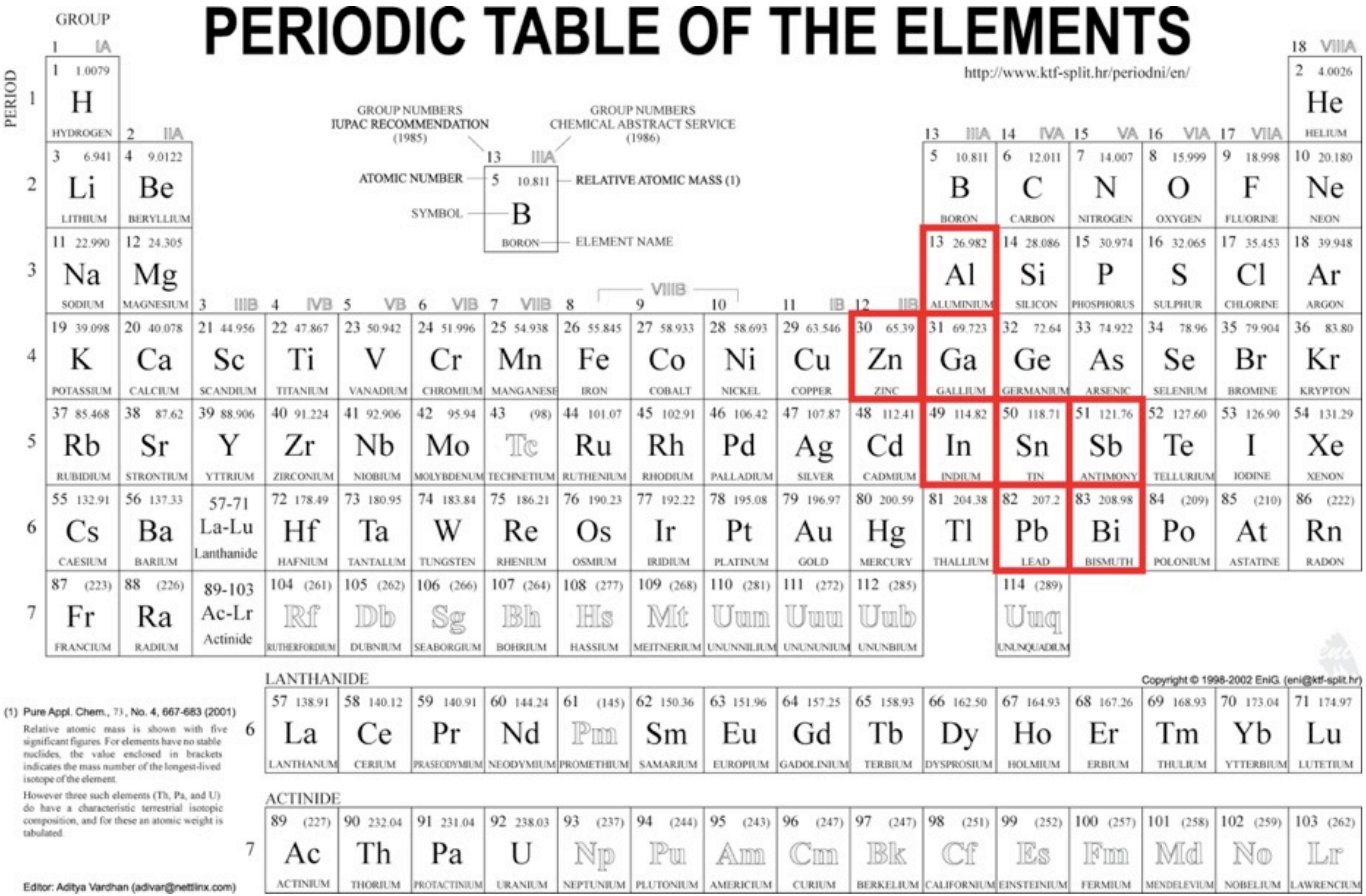
Should have low melting point

High solubility

Low reactivity with the crucible

Does not incorporate into the crystal

Commonly used fluxes to grow metallic crystals



PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

GROUP NUMBERS IUPAC RECOMMENDATION (1985)

GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)

ATOMIC NUMBER — 5 10.811 — RELATIVE ATOMIC MASS (1)

SYMBOL — B

BORON — ELEMENT NAME

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

6	57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

7	89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)

Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

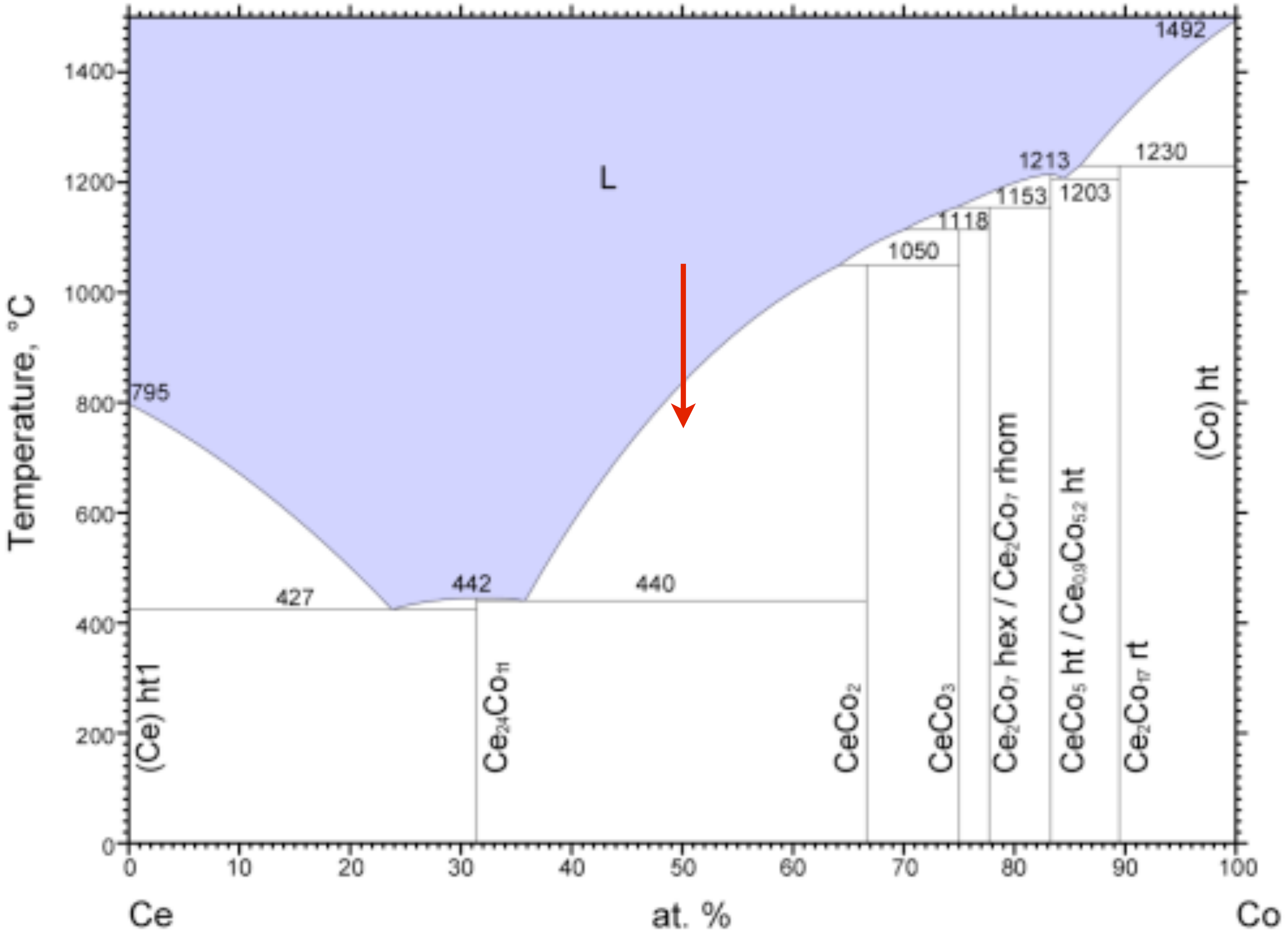
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

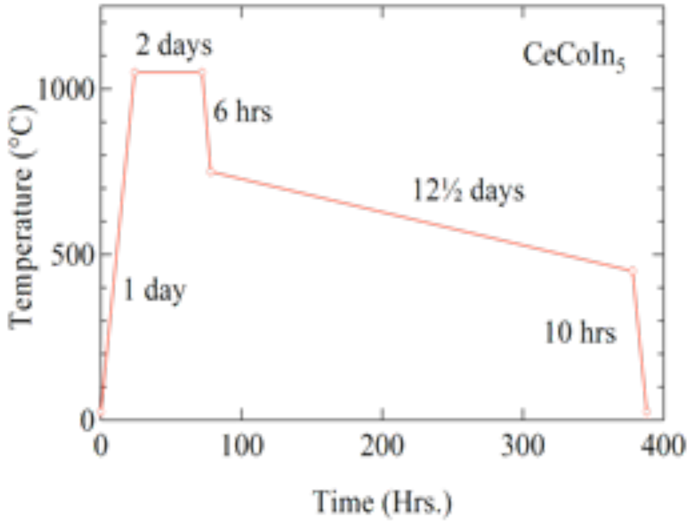
Editor: Aditya Vardhan (adivar@nettlinx.com)

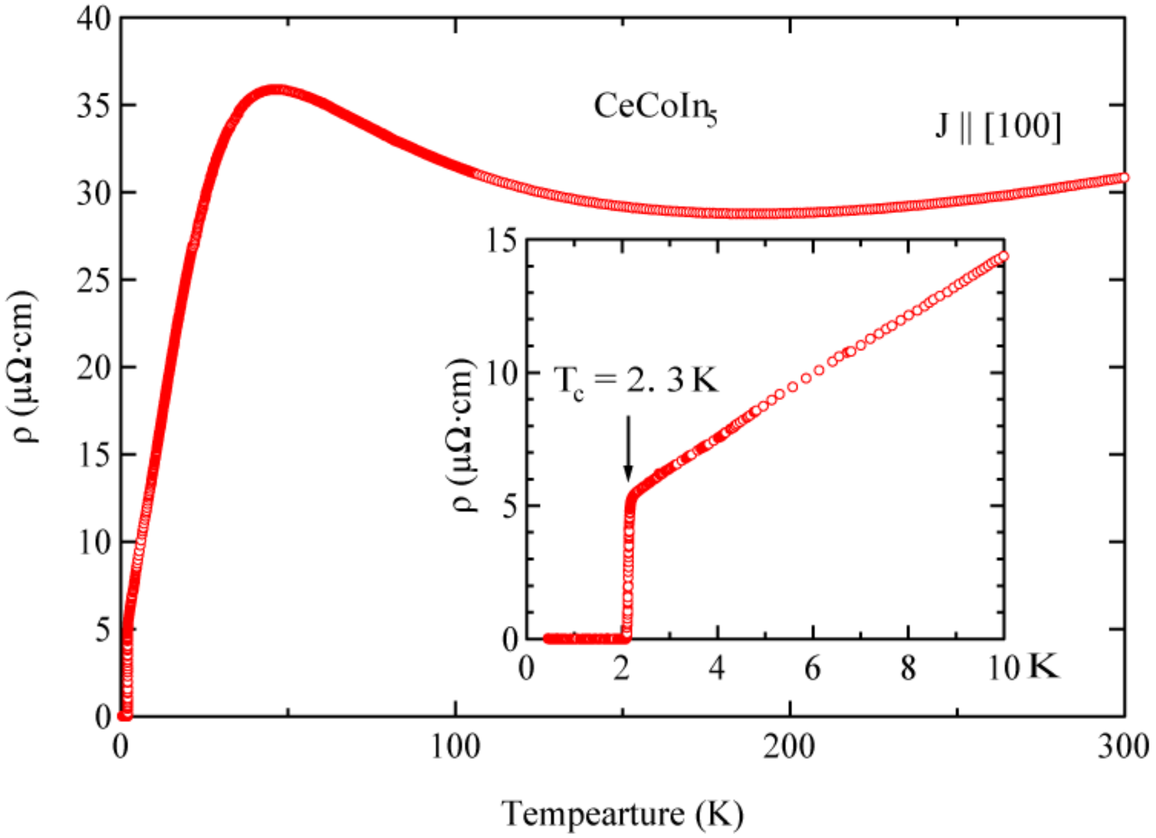
Flux growth example: $CeCoIn_5$

Starting composition

Ce : Co : In
1 : 1 : 24



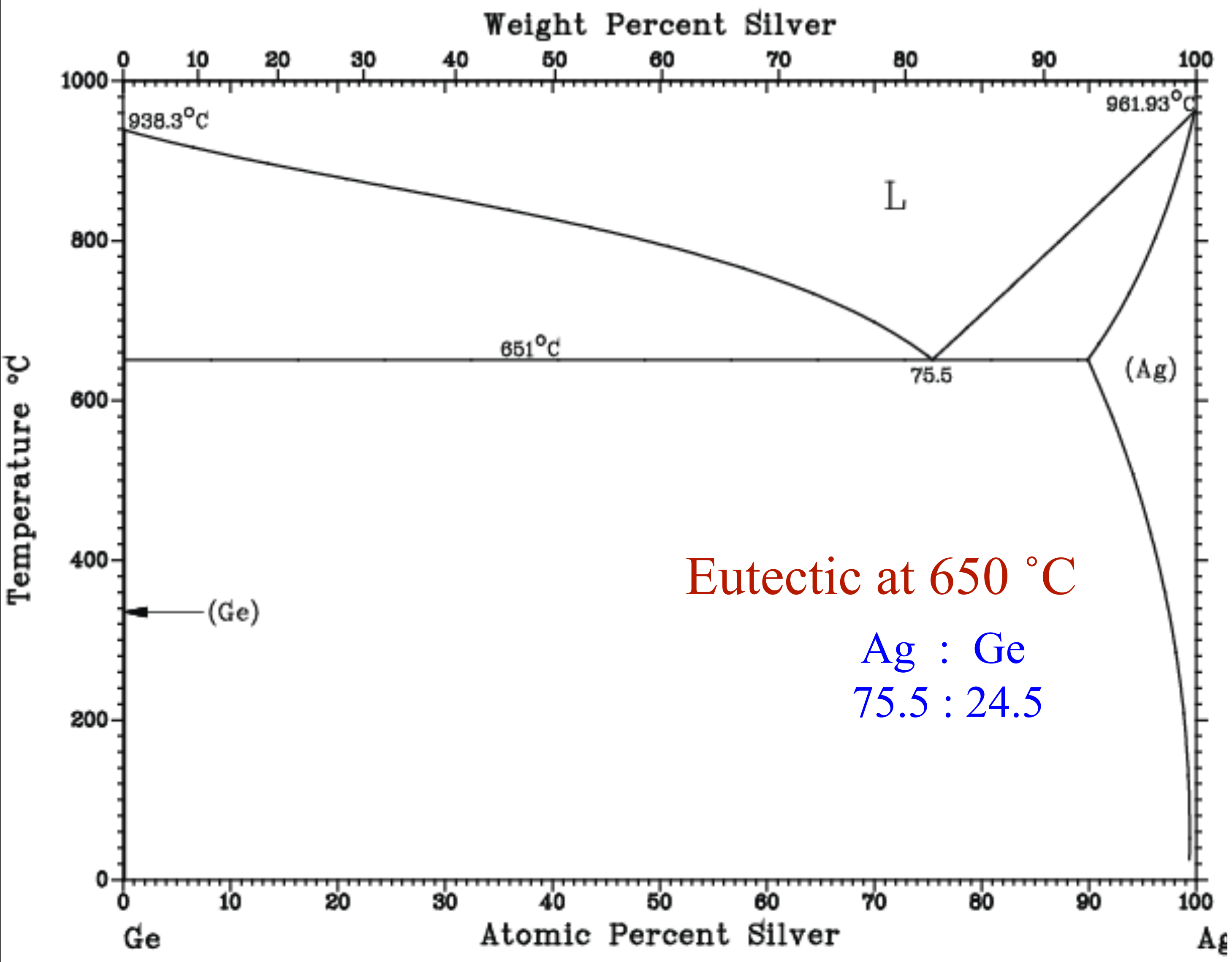




Flux growth of $CeAg_2Ge_2$

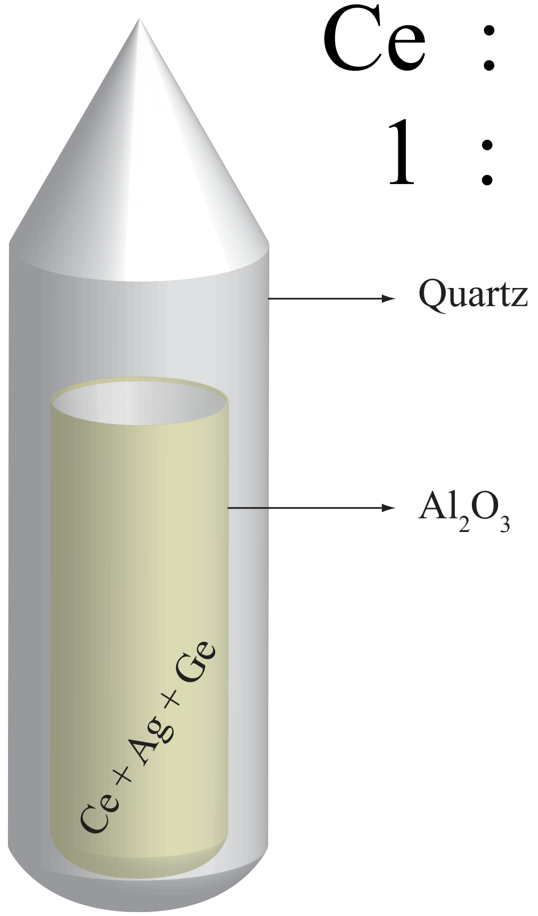
Individual metals of Ce, Ag and Ge

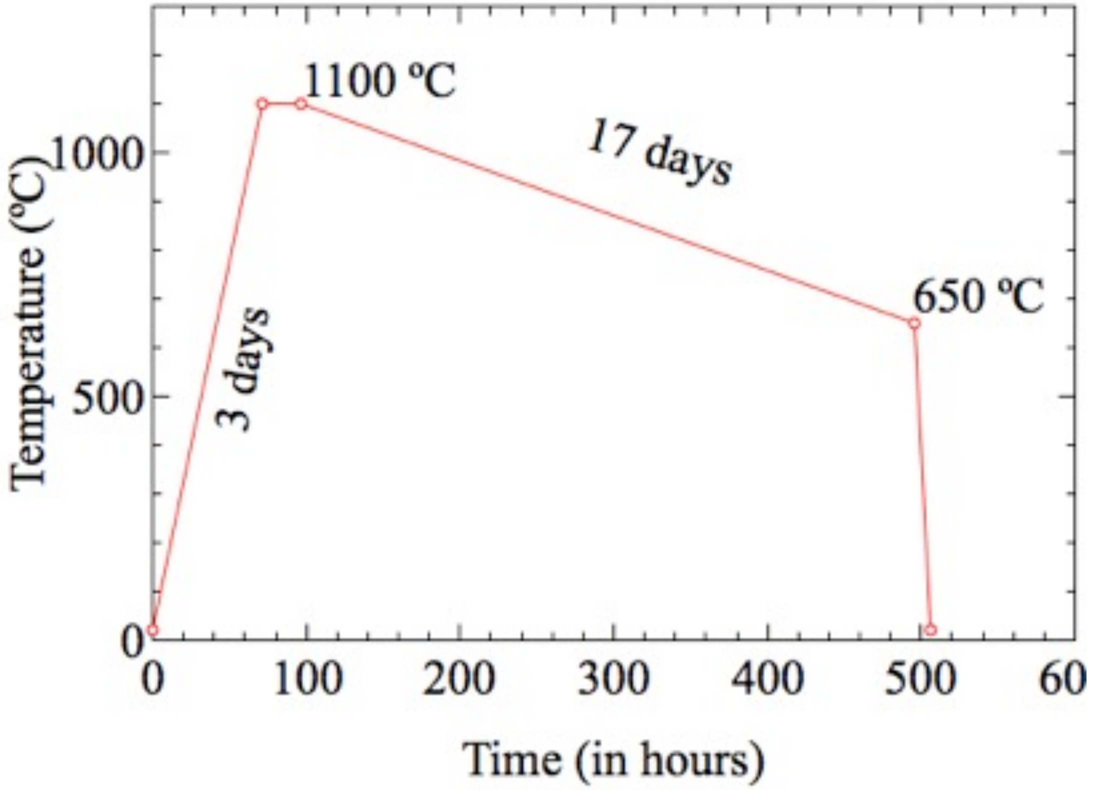
Ce : Ag : Ge
1 : 16 : 7



Eutectic at 650 ˚C

Ag : Ge
75.5 : 24.5



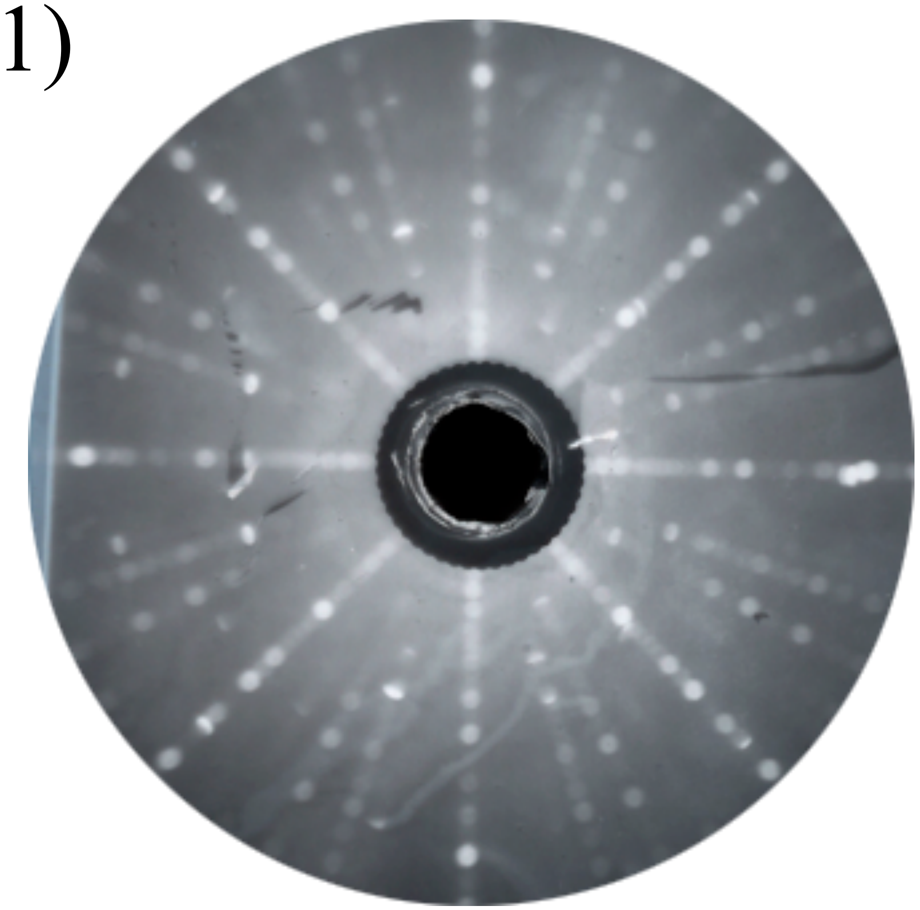


$CeAg_2Ge_2$ Single crystals

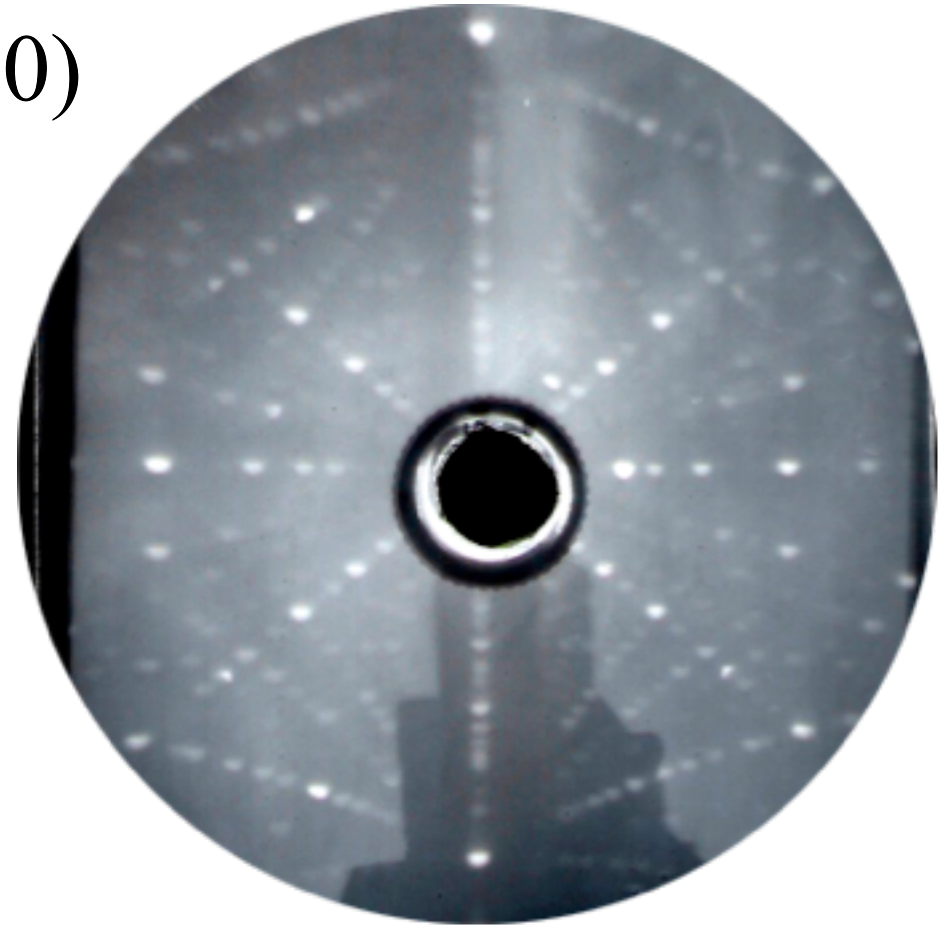
10 mm x 8 mm x 2mm

The flat plane of the crystal corresponds to (001)

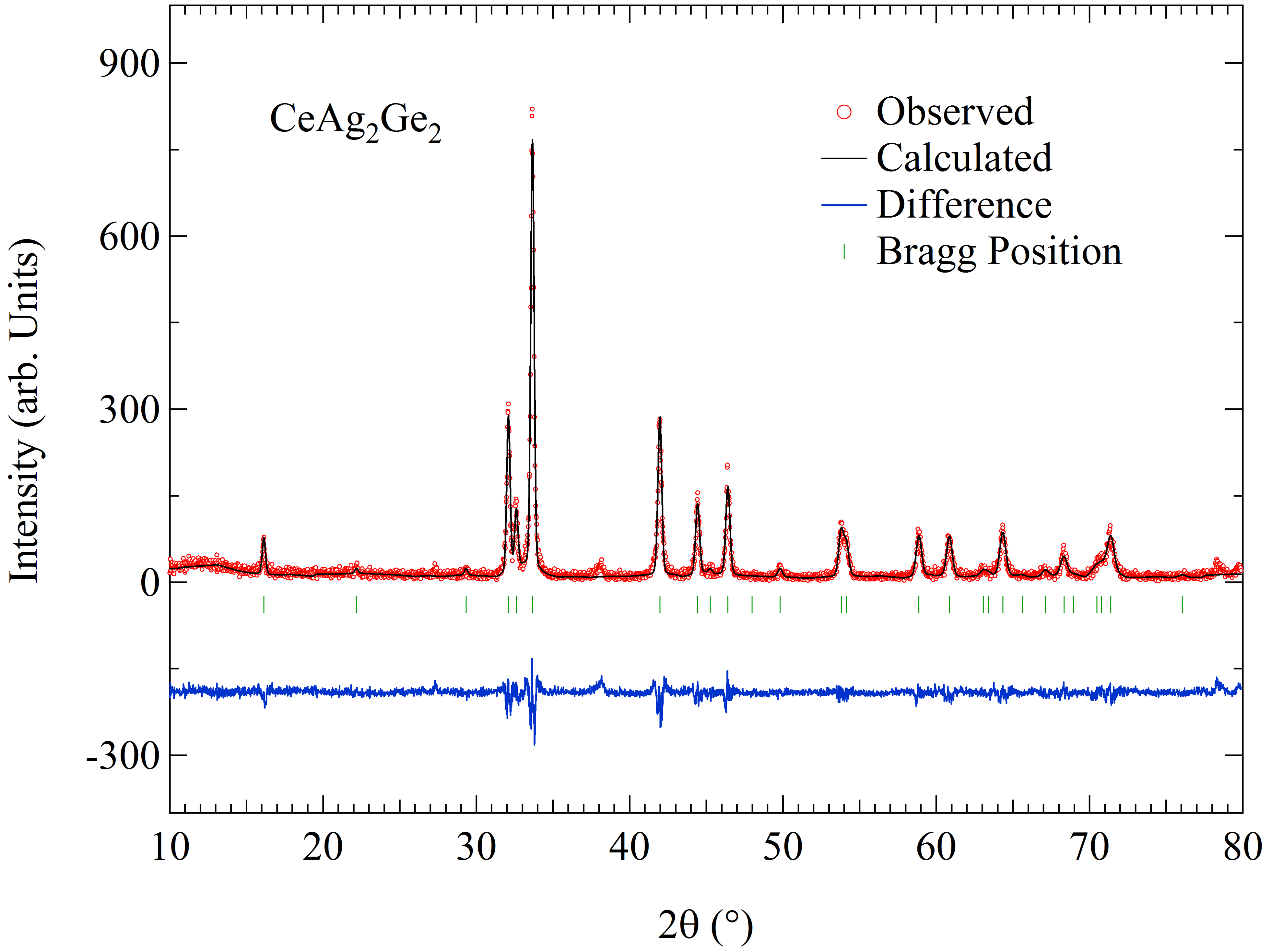
(001)



(100)



Powder X-ray Diffraction

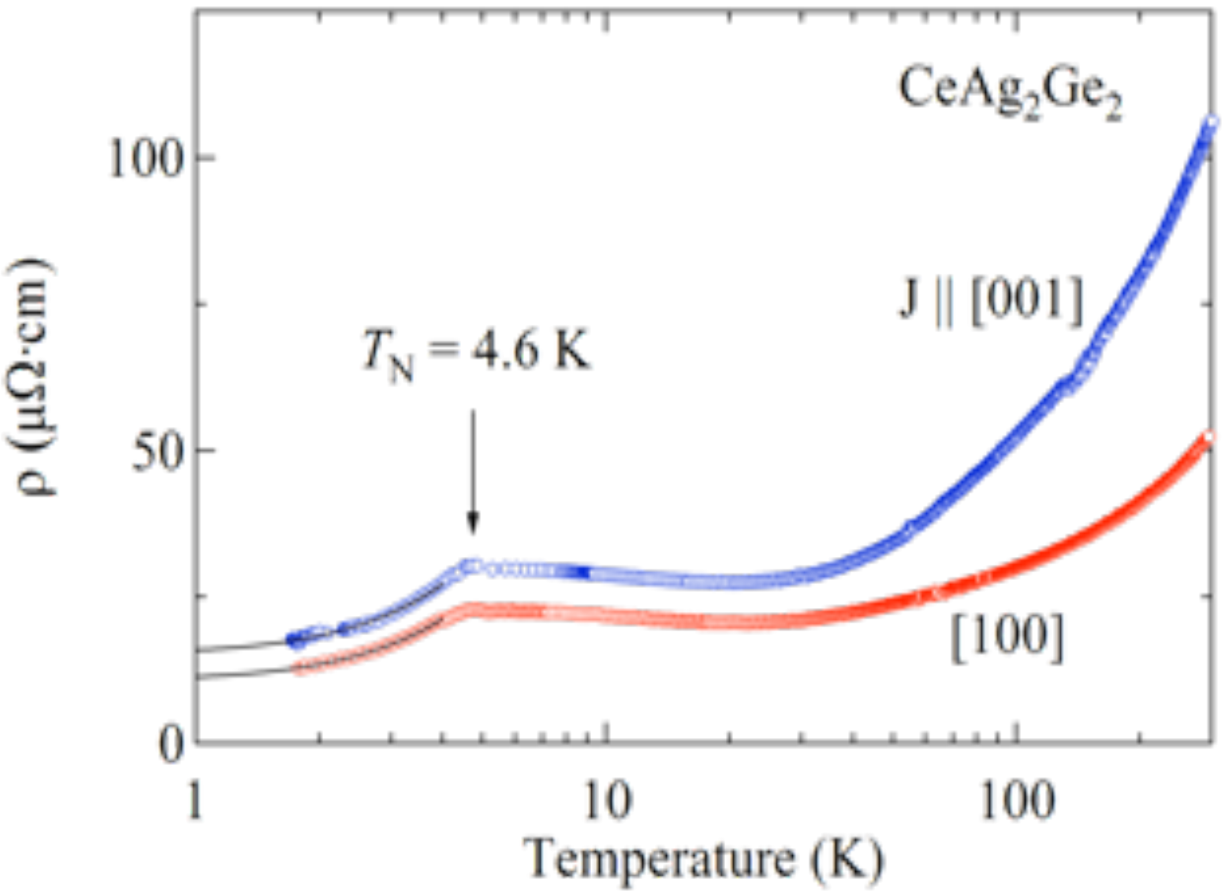


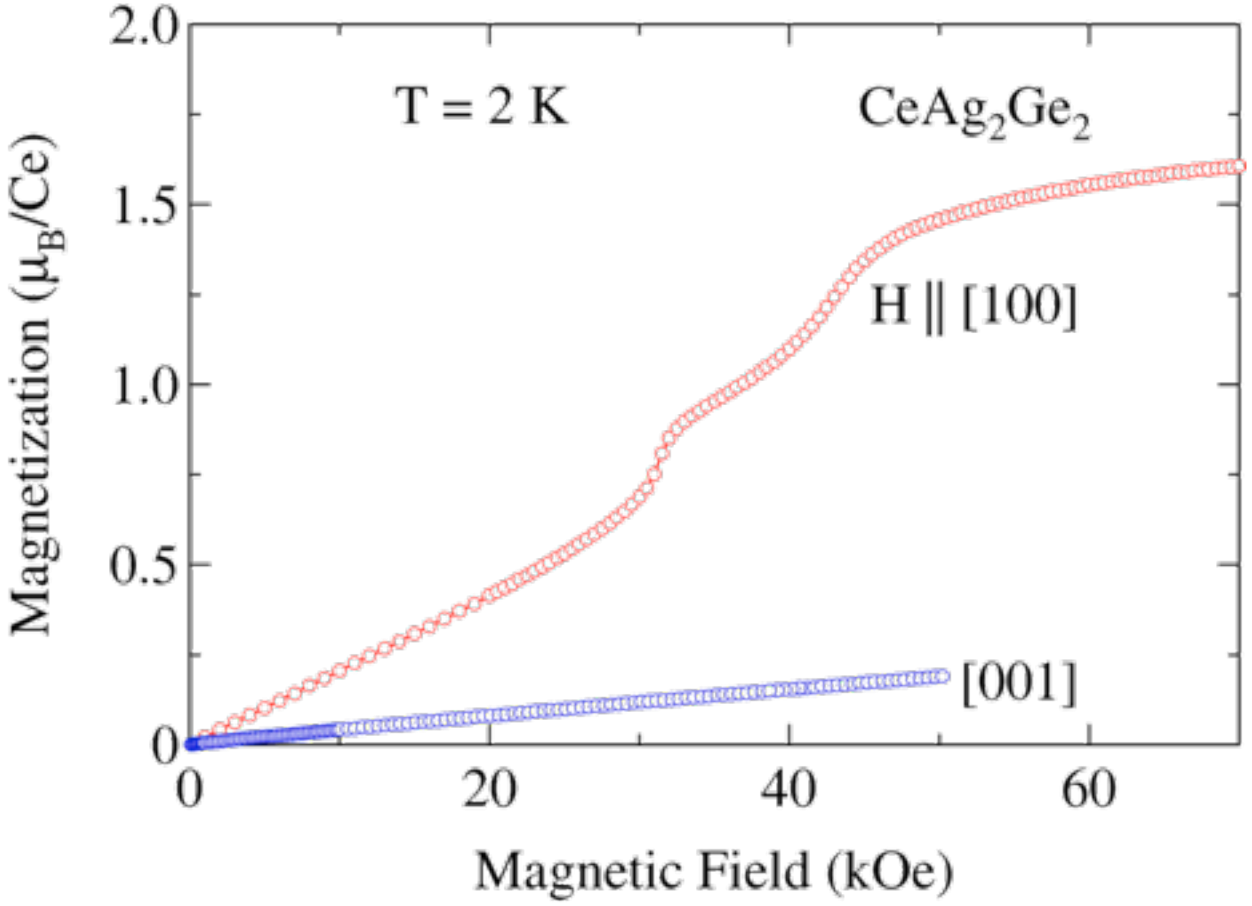
a = 4.307 Å

c = 10.973 Å

EDAX measurement also confirmed the stoichiometry

Magnetic properties of $CeAg_2Ge_2$





Pnictide superconductors

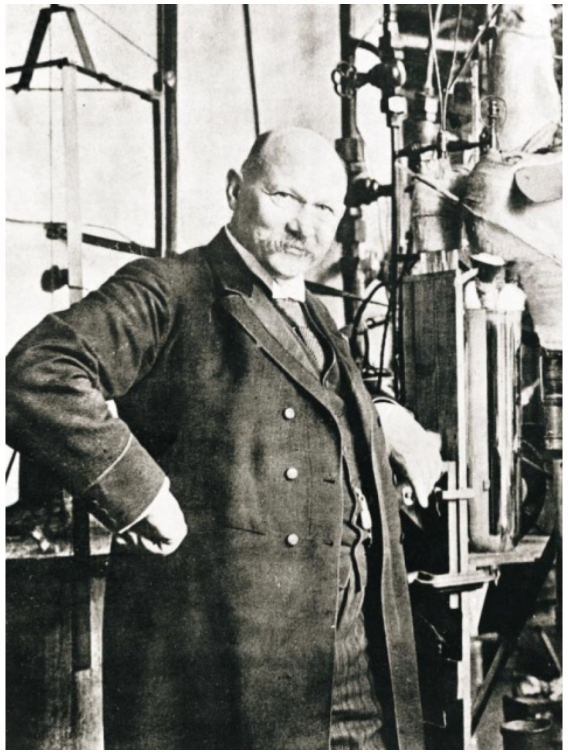
1908 Liquefaction of He

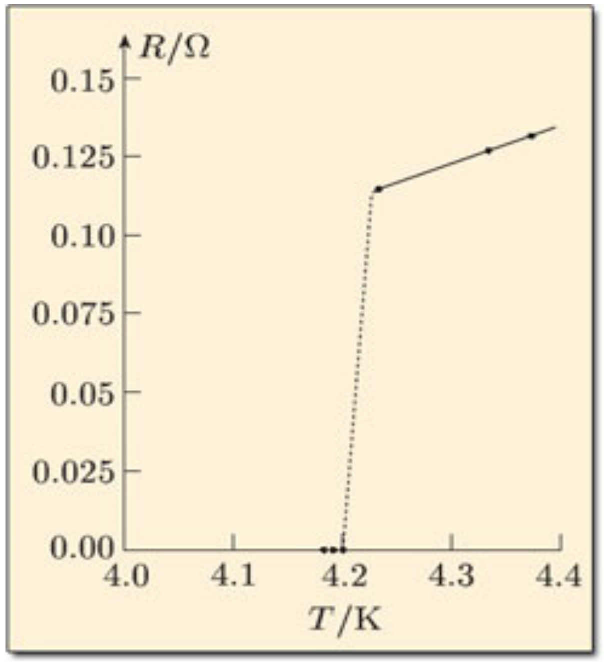
1911

Superconductivity

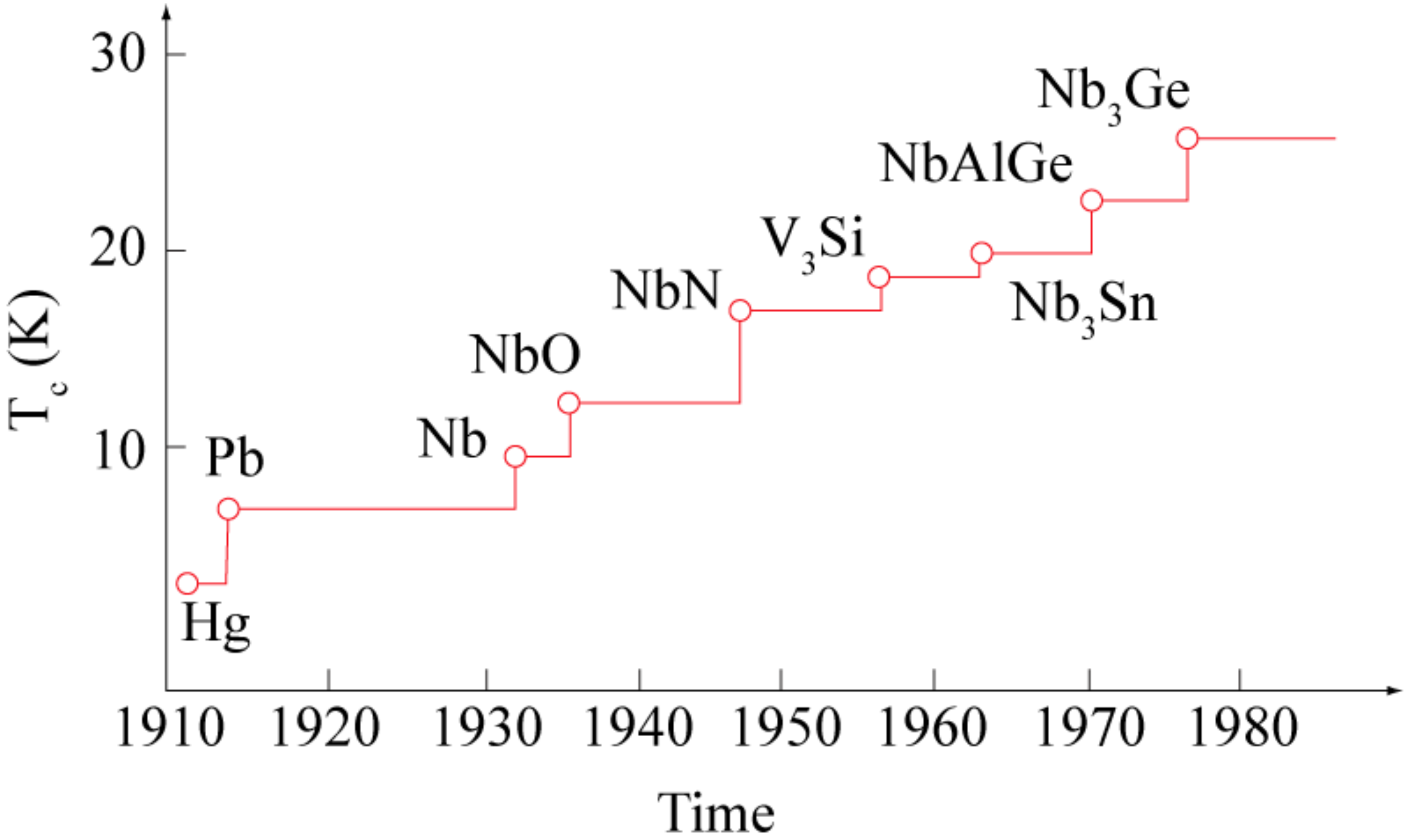
2011
100 Years

Heike Kamerlingh Onnes



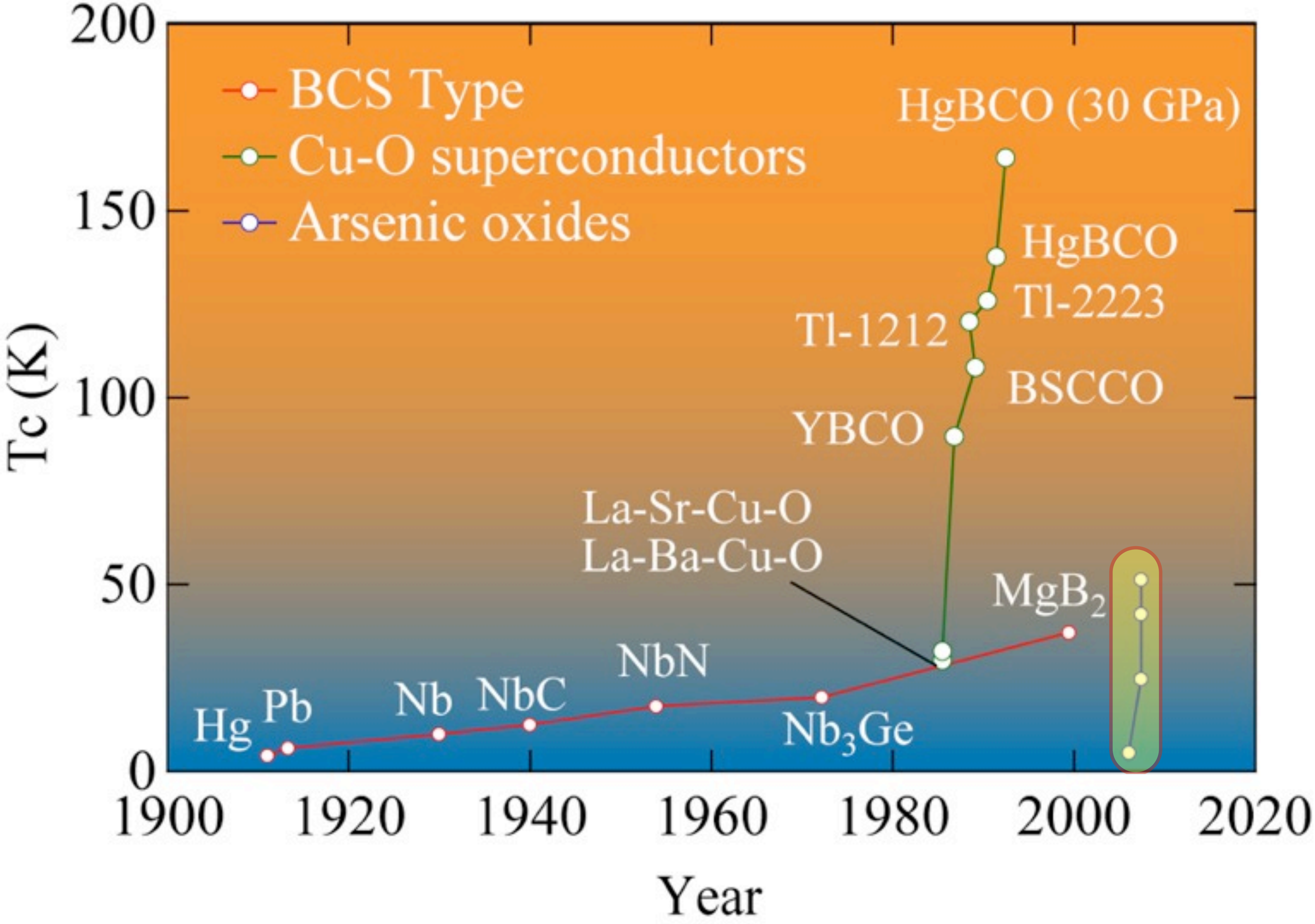


1973
Tc = 22 - 23 K in Nb_3Ge



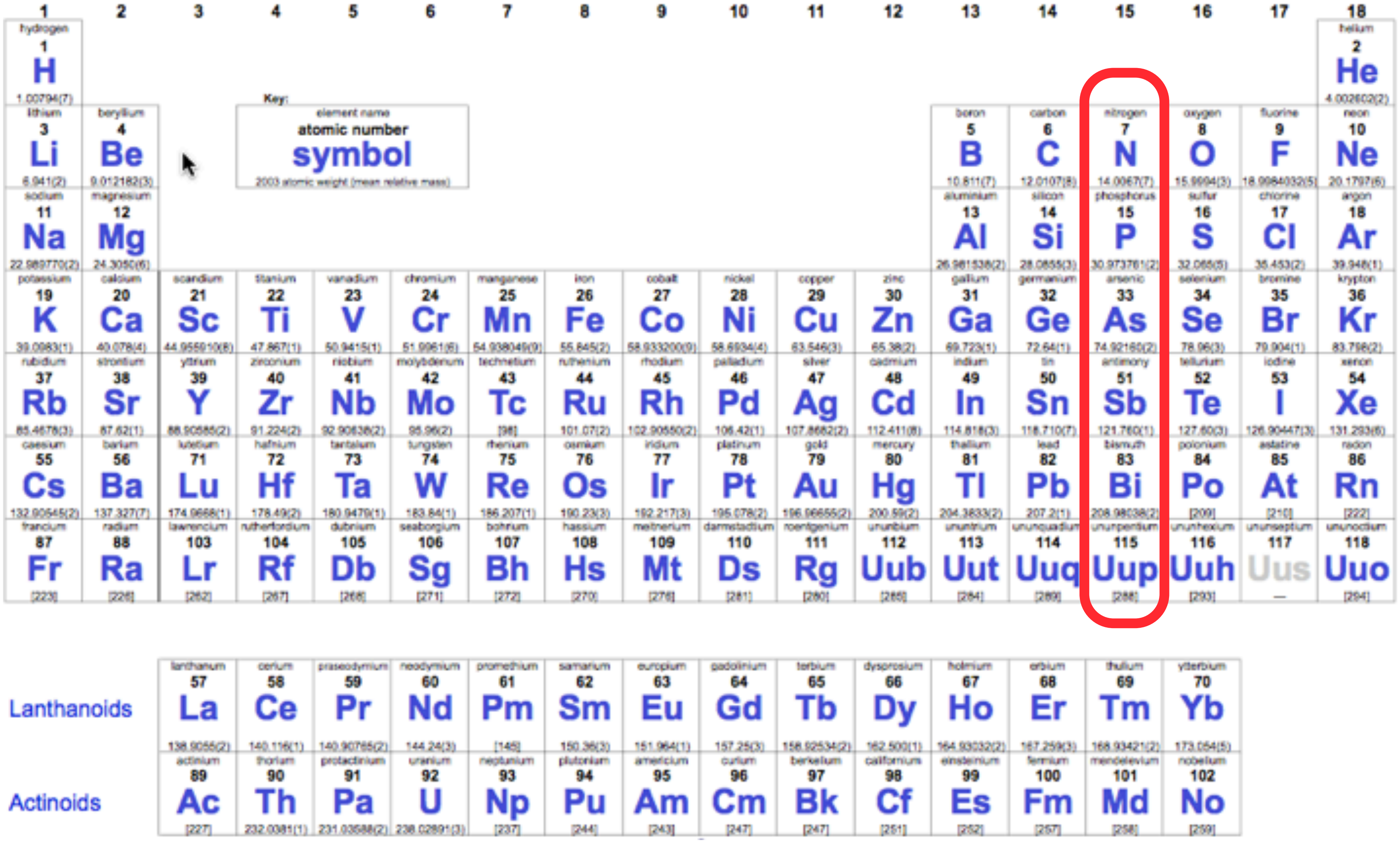
Oxides and non-transition metals were not serious contenders for High Tc

Oxide superconductors



Pnictides Greek : Choking or suffocation

Group V elements

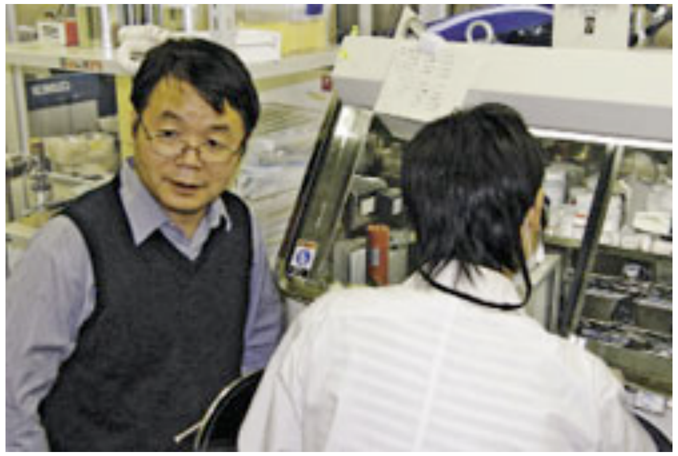


1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 H																	helium 2 He
lithium 3 Li	beryllium 4 Be											boron 5 B	carbon 6 C	nitrogen 7 N	oxygen 8 O	fluorine 9 F	neon 10 Ne
sodium 11 Na	magnesium 12 Mg											aluminium 13 Al	silicon 14 Si	phosphorus 15 P	sulfur 16 S	chlorine 17 Cl	argon 18 Ar
potassium 19 K	calcium 20 Ca	scandium 21 Sc	titanium 22 Ti	vanadium 23 V	chromium 24 Cr	manganese 25 Mn	iron 26 Fe	cobalt 27 Co	nickel 28 Ni	copper 29 Cu	zinc 30 Zn	gallium 31 Ga	germanium 32 Ge	arsenic 33 As	selenium 34 Se	bromine 35 Br	krypton 36 Kr
rubidium 37 Rb	strontium 38 Sr	yttrium 39 Y	zirconium 40 Zr	niobium 41 Nb	molybdenum 42 Mo	technetium 43 Tc	ruthenium 44 Ru	rhodium 45 Rh	palladium 46 Pd	silver 47 Ag	cadmium 48 Cd	indium 49 In	tin 50 Sn	antimony 51 Sb	tellurium 52 Te	iodine 53 I	xenon 54 Xe
caesium 55 Cs	barium 56 Ba	lutetium 71 Lu	hafnium 72 Hf	tantalum 73 Ta	tungsten 74 W	rhenium 75 Re	osmium 76 Os	iridium 77 Ir	platinum 78 Pt	gold 79 Au	mercury 80 Hg	thallium 81 Tl	lead 82 Pb	bismuth 83 Bi	polonium 84 Po	astatine 85 At	radon 86 Rn
francium 87 Fr	radium 88 Ra	lawrencium 103 Lr	rutherfordium 104 Rf	dubnium 105 Db	seaborgium 106 Sg	bohrium 107 Bh	hassium 108 Hs	meitnerium 109 Mt	darmstadtium 110 Ds	roentgenium 111 Rg	ununbium 112 Uub	ununtrium 113 Uut	ununquadium 114 Uuq	ununpentium 115 Uup	ununhexium 116 Uuh	ununseptium 117 Uus	ununoctium 118 Uuo

Key:
element name
atomic number
symbol
2003 atomic weight (mean relative mass)

Lanthanoids	lanthanum 57 La	cerium 58 Ce	praseodymium 59 Pr	neodymium 60 Nd	promethium 61 Pm	samarium 62 Sm	europium 63 Eu	gadolinium 64 Gd	terbium 65 Tb	dysprosium 66 Dy	holmium 67 Ho	erbium 68 Er	thulium 69 Tm	ytterbium 70 Yb
Actinoids	actinium 89 Ac	thorium 90 Th	protactinium 91 Pa	uranium 92 U	neptunium 93 Np	plutonium 94 Pu	americium 95 Am	curium 96 Cm	berkelium 97 Bk	californium 98 Cf	einsteinium 99 Es	fermium 100 Fm	mendelevium 101 Md	nobelium 102 No

Prof. Hideo Hosono



March 2006

Tc = 4 K

J|A|C|S
COMMUNICATIONS

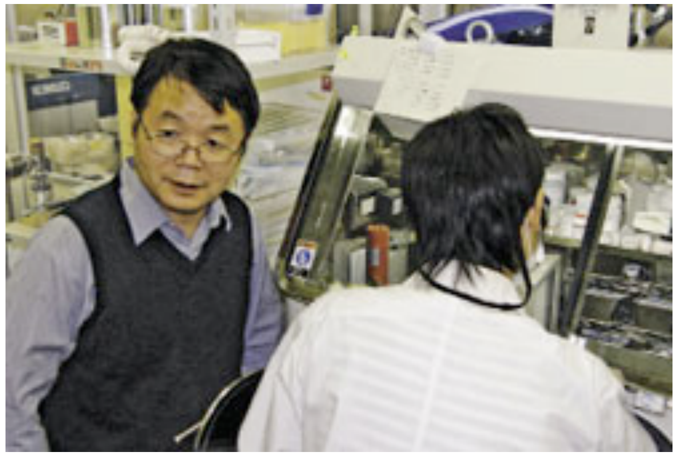
Iron-Based Layered Superconductor: LaOFeP

Yoichi Kamihara,[†] Hidenori Hiramatsu,[†] Masahiro Hirano,[†,‡] Ryuto Kawamura,[§] Hiroshi Yanagi,[§]
Toshio Kamiya,[†,§] and Hideo Hosono[*,†,‡]

ERATO-SORST, JST, Frontier Collaborative Research Center, Tokyo Institute of Technology, Mail Box S2-13, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, Frontier Collaborative Research Center, Tokyo Institute of Technology, Mail Box S2-13, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, and Materials and Structures Laboratory, Tokyo Institute of Technology, Mail Box R3-4, 4259 Nagatsuta, Yokohama 226-8503, Japan

Received May 15, 2006; E-mail: hosono@msl.titech.ac.jp

Prof. Hideo Hosono



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Tc = 4 K

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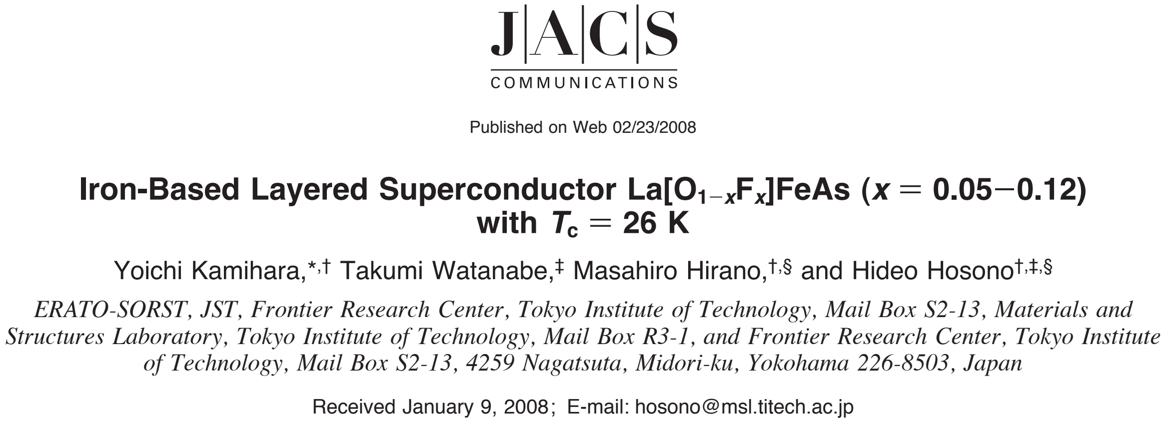
Received May 15, 2006; E-mail: hosono@msl.titech.ac.jp

Feb. 2008

Tc = 26 K



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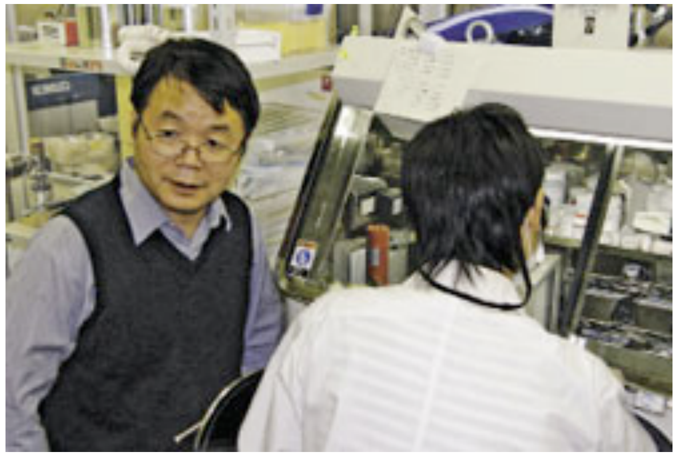
Iron-Based Layered Superconductor La[O$_{1-x}$F$_x$]FeAs ($x = 0.05-0.12$) with $T_c = 26$ K

Yoichi Kamihara,*[,†] Takumi Watanabe,[‡] Masahiro Hirano,[†,§] and Hideo Hosono[†,‡,§]

ERATO-SORST, JST, Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, Materials and Structures Laboratory, Tokyo Institute of Technology, Mail Box R3-1, and Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received January 9, 2008; E-mail: hosono@msl.titech.ac.jp

Prof. Hideo Hosono



March 2006

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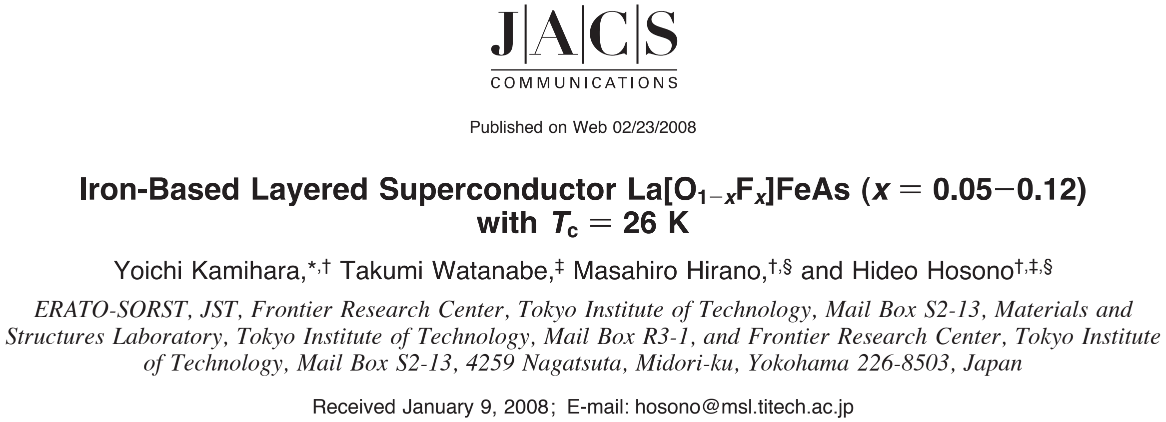

J|A|C|S COMMUNICATIONS

Published on Web 02/23/2008

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Yoichi Kamihara,*[,†] Takumi Watanabe,[‡] Masahiro Hirano,[†,§] and Hideo Hosono[†,‡,§]

ERATO-SORST, JST, Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, Materials and Structures Laboratory, Tokyo Institute of Technology, Mail Box R3-1, and Frontier Research Center, Tokyo Institute of Technology, Mail Box S2-13, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received January 9, 2008; E-mail: hosono@msl.titech.ac.jp

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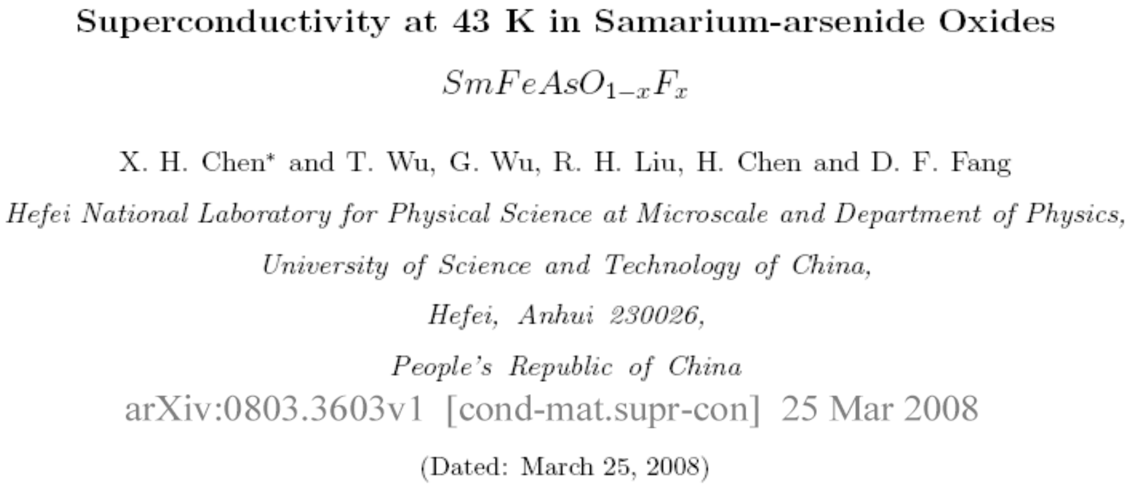


Superconductivity at 43 K in Samarium-arsenide Oxides $SmFeAsO_{1-x}F_x$

X. H. Chen* and T. Wu, G. Wu, R. H. Liu, H. Chen and D. F. Fang

Hefei National Laboratory for Physical Science at Microscale and Department of Physics,
University of Science and Technology of China,
Hefei, Anhui 230026,
People's Republic of China

arXiv:0803.3603v1 [cond-mat.supr-con] 25 Mar 2008

(Dated: March 25, 2008)

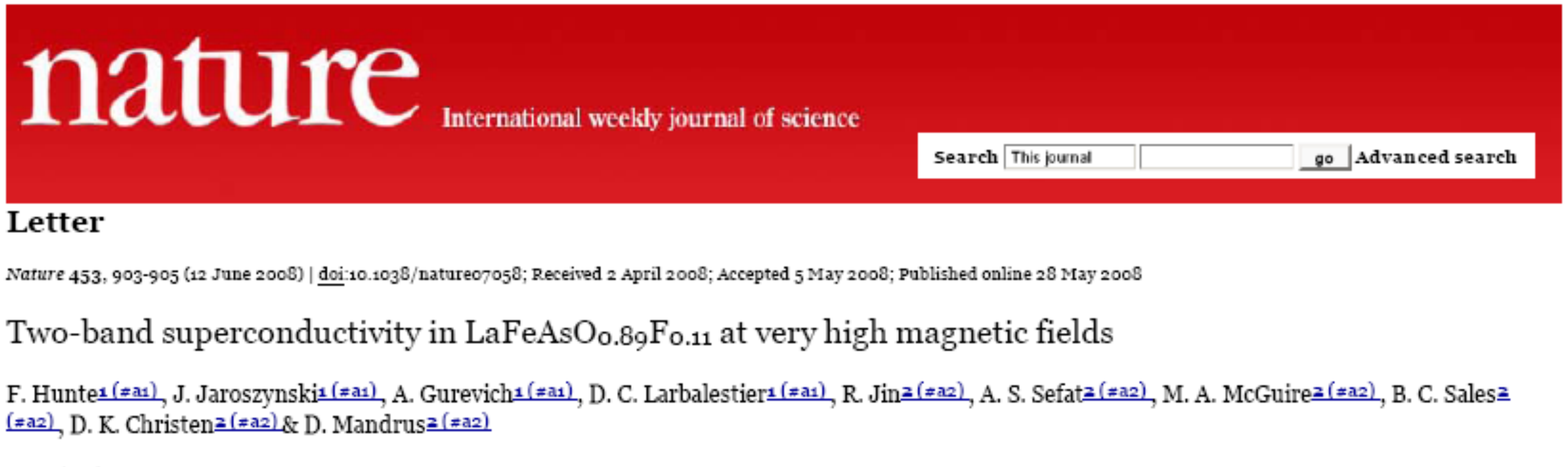
Prof. Hideo Hosono


nature International weekly journal of science

Letter

Nature 459, 64-67 (7 May 2009) | doi:10.1038/nature07981; Received 4 November 200

A large iron isotope effect in SmFeAsO$_{1-x}$F$_x$ an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Nature 453, 903-905 (12 June 2008) | doi:10.1038/nature07058; Received 2 April 2008; Accepted 5 May 2008; Published online 28 May 2008

Two-band superconductivity in LaFeAsO$_{0.89}$F$_{0.11}$ at very high magnetic fields

F. Hunte[1] (#a1), J. Jaroszynski[1] (#a1), A. Gurevich[1] (#a1), D. C. Larbalestier[1] (#a1), R. Jin[2] (#a2), A. S. Sefat[2] (#a2), M. A. McGuire[2] (#a2), B. C. Sales[2] (#a2), D. K. Christen[2] (#a2) & D. Mandrus[2] (#a2)

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2. Materials


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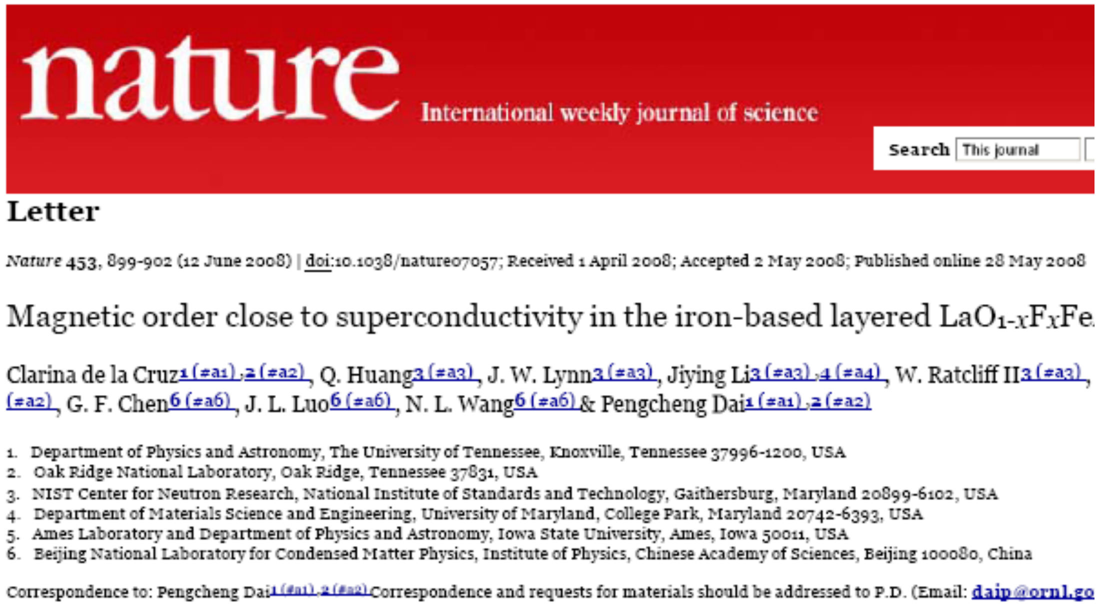
Nature 453, 1224-1227 (26 June 2008) | doi:10.1038/nature07081; Received 23 April 2008; Accepted 5 May 2008; Published online 4 Jun

A BCS-like gap in the superconductor SmFeAsO$_{0.85}$F$_{0.15}$

T. Y. Chen[1] (#a1), Z. Tesanovic[1] (#a1), R. H. Liu[2] (#a2), X. H. Chen[2] (#a2) & C. L. Chien[1] (#a1)

1. Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland 21218, USA
2. Hefei National Laboratory for Physical Sciences at Microscale and Department of Physics, University of Science and Technology of Chir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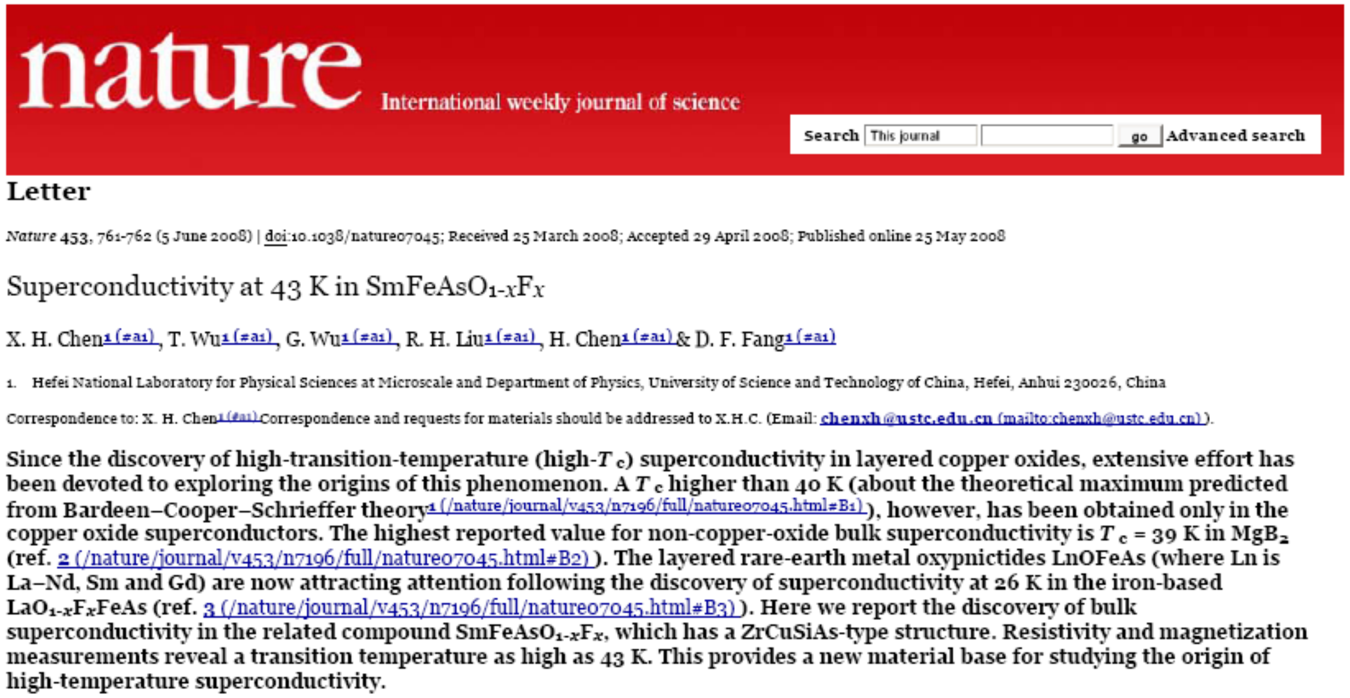
Nature 453, 899-902 (12 June 2008) | doi:10.1038/nature07057; Received 1 April 2008; Accepted 2 May 2008; Published online 28 May 2008

Magnetic order close to superconductivity in the iron-based layered LaO$_{1-x}$F$_x$Fe

Clarina de la Cruz[1] (#a1), [2] (#a2), Q. Huang[3] (#a3), J. W. Lynn[3] (#a3), Jiying Li[3] (#a3), [4] (#a4), W. Ratcliff II[3] (#a3), (#a2), G. F. Chen[6] (#a6), J. L. Luo[6] (#a6), N. L. Wang[6] (#a6) & Pengcheng Dai[1] (#a1), [2] (#a2)

1. Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200, USA
2. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
3. NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, USA
4. Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742-6393, USA
5. Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA
6. Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Correspondence to: Pengcheng Dai[1] (#a1), [2] (#a2) Correspondence and requests for materials should be addressed to P.D. (Email: daip@ornl.go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Letter

Nature 453, 761-762 (5 June 2008) | doi:10.1038/nature07045; Received 25 March 2008; Accepted 29 April 2008; Published online 25 May 2008

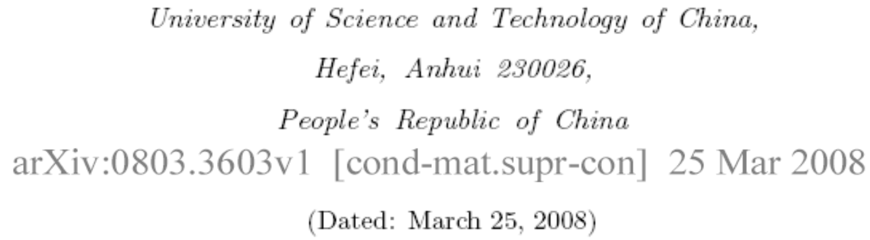
Superconductivity at 43 K in SmFeAsO$_{1-x}$F$_x$

X. H. Chen[1] (#a1), T. Wu[1] (#a1), G. Wu[1] (#a1), R. H. Liu[1] (#a1), H. Chen[1] (#a1) & D. F. Fang[1] (#a1)

1. Hefei National Laboratory for Physical Sciences at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

Correspondence to: X. H. Chen[1] (#a1) Correspondence and requests for materials should be addressed to X.H.C. (Email: chenxh@ustc.edu.cn (mailto:chenxh@ustc.edu.cn)).

Since the discovery of high-transition-temperature (high-T_c) superconductivity in layered copper oxides, extensive effort has been devoted to exploring the origins of this phenomenon. A T_c higher than 40 K (about the theoretical maximum predicted from Bardeen–Cooper–Schrieffer theory[1 (/nature/journal/v453/n7196/full/nature07045.html#B1)]), however, has been obtained only in the copper oxide superconductors. The highest reported value for non-copper-oxide bulk superconductivity is T_c = 39 K in MgB$_2$ (ref. 2 (/nature/journal/v453/n7196/full/nature07045.html#B2)). The layered rare-earth metal oxypnictides LnOFeAs (where Ln is La–Nd, Sm and Gd) are now attracting attention following the discovery of superconductivity at 26 K in the iron-based LaO$_{1-x}$F$_x$FeAs (ref. 3 (/nature/journal/v453/n7196/full/nature07045.html#B3)). Here we report the discovery of bulk superconductivity in the related compound SmFeAsO$_{1-x}$F$_x$, which has a ZrCuSiAs-type structure. Resistivity and magnetization measurements reveal a transition temperature as high as 43 K. This provides a new material base for studying the origin of high-temperature superconductivity.


University of Science and Technology of China,

Hefei, Anhui 230026,

People's Republic of China

arXiv:0803.3603v1 [cond-mat.supr-con] 25 Mar 2008

(Dated: March 25, 2008)

Prof. Hideo Hosono

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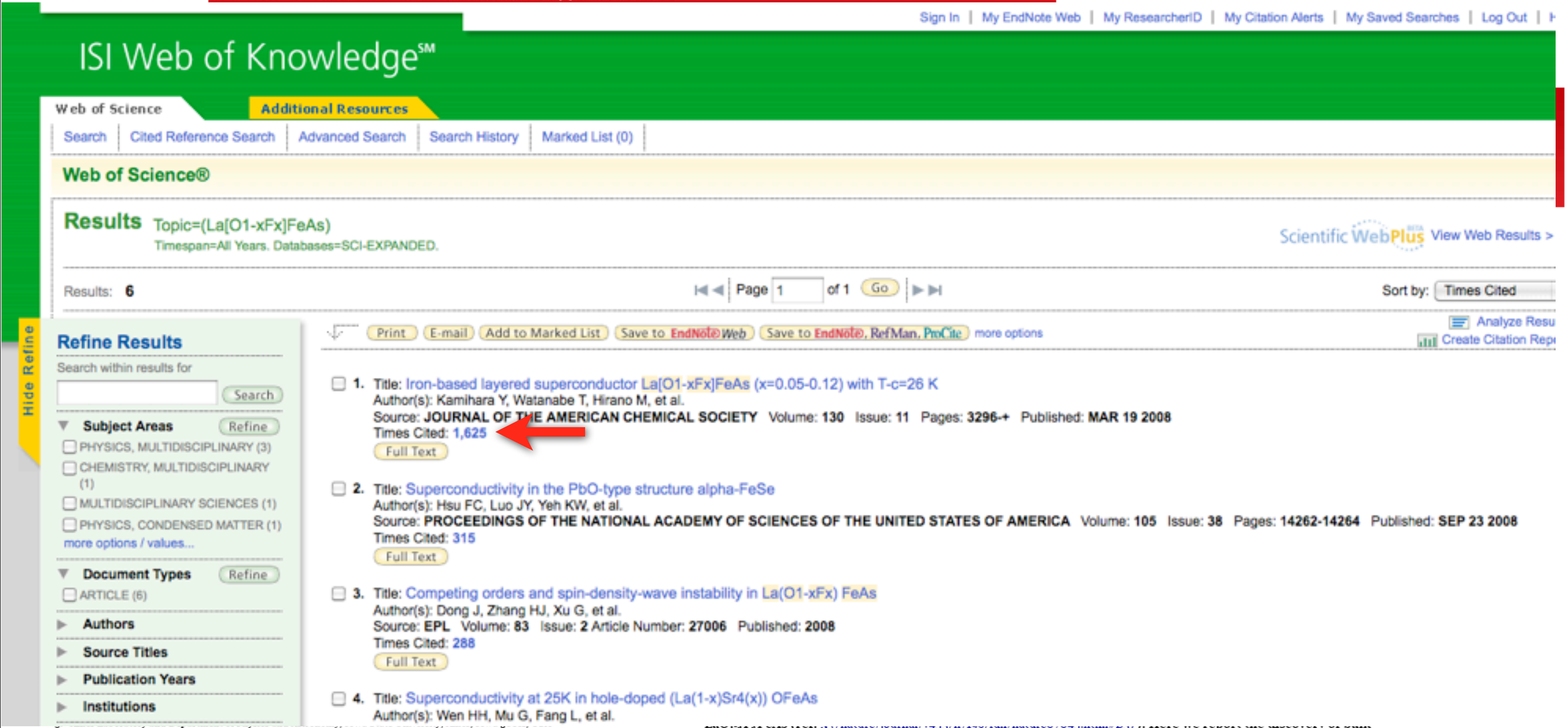

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☐ **1.** Title: Iron-based layered superconductor La[O1-xFx]FeAs (x=0.05-0.12) with T-c=26 K
Author(s): Kamihara Y, Watanabe T, Hirano M, et al.
Source: **JOURNAL OF THE AMERICAN CHEMICAL SOCIETY** Volume: **130** Issue: **11** Pages: **3296-+** Published: **MAR 19 2008**
Times Cited: 1,625

☐ **2.** Title: Superconductivity in the PbO-type structure alpha-FeSe
Author(s): Hsu FC, Luo JY, Yeh KW, et al.
Source: **PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES OF THE UNITED STATES OF AMERICA** Volume: **105** Issue: **38** Pages: **14262-14264** Published: **SEP 23 2008**
Times Cited: 315

☐ **3.** Title: Competing orders and spin-density-wave instability in La(O1-xFx) FeAs
Author(s): Dong J, Zhang HJ, Xu G, et al.
Source: **EPL** Volume: **83** Issue: **2** Article Number: **27006** Published: **2008**
Times Cited: 288

☐ **4.** Title: Superconductivity at 25K in hole-doped (La(1-x)Sr4(x)) OFeAs
Author(s): Wen HH, Mu G, Fang L, et al.

6. Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Correspondence to: Pengcheng Dai[1 (#a1), 2 (#a2)] Correspondence and requests for materials should be addressed to P.D. (Email: daip@ornl.go

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University of Science and Technology of China,

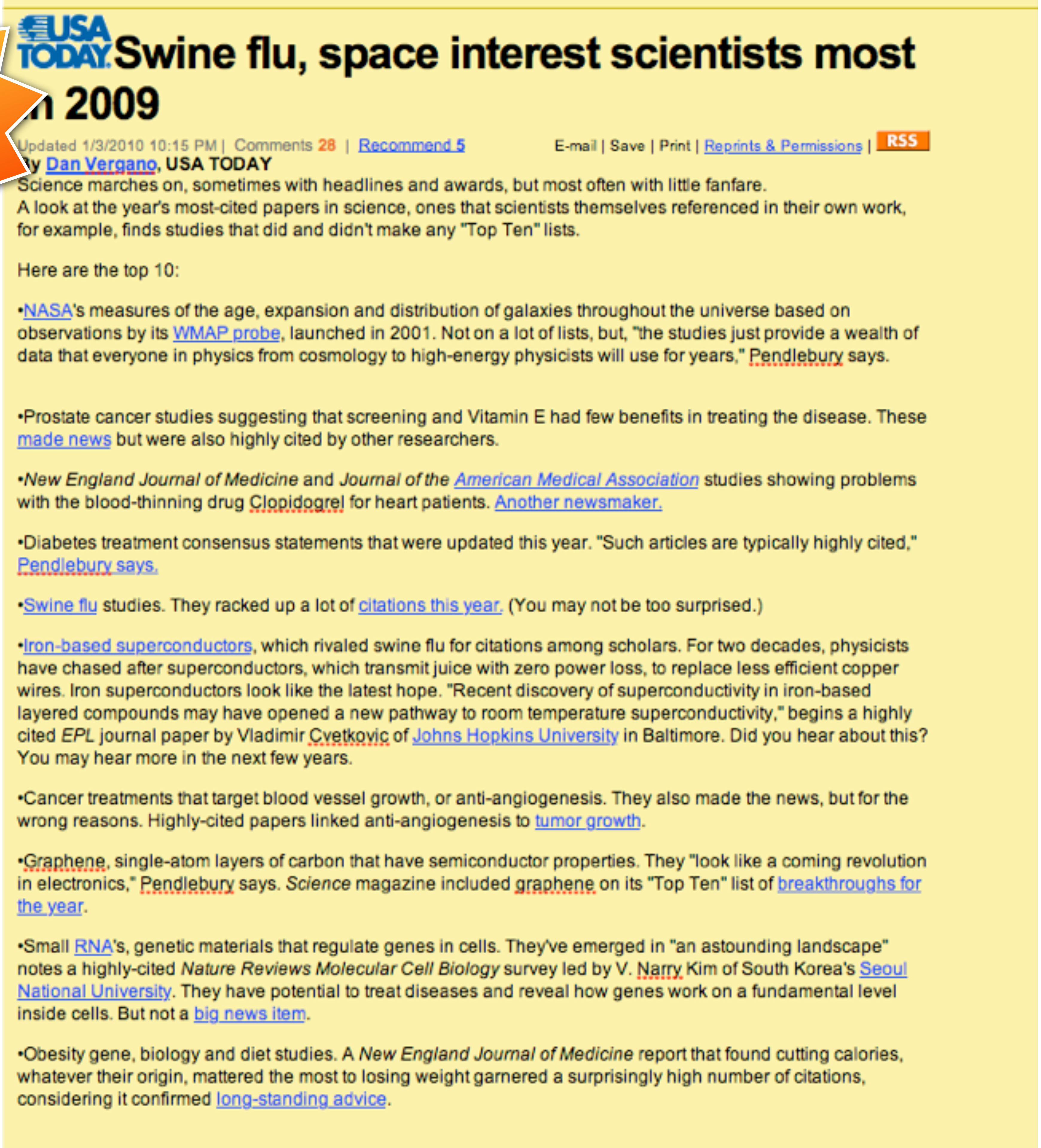
Hefei, Anhui 230026,

People's Republic of China

arXiv:0803.3603v1 [cond-mat.supr-con] 25 Mar 2008

(Dated: March 25, 2008)

Top Ten
most cited articles
in 2009



USA TODAY

Swine flu, space interest scientists most n 2009

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y Dan Vergano, USA TODAY

Science marches on, sometimes with headlines and awards, but most often with little fanfare.

A look at the year's most-cited papers in science, ones that scientists themselves referenced in their own work, for example, finds studies that did and didn't make any "Top Ten" lists.

Here are the top 10:

1 •NASA's measures of the age, expansion and distribution of galaxies throughout the universe based on observations by its WMAP probe, launched in 2001. Not on a lot of lists, but, "the studies just provide a wealth of data that everyone in physics from cosmology to high-energy physicists will use for years," Pendlebury says.

2 •Prostate cancer studies suggesting that screening and Vitamin E had few benefits in treating the disease. These made news but were also highly cited by other researchers.

3 •*New England Journal of Medicine* and *Journal of the American Medical Association* studies showing problems with the blood-thinning drug Clopidogrel for heart patients. Another newsmaker.

4 •Diabetes treatment consensus statements that were updated this year. "Such articles are typically highly cited," Pendlebury says.

5 •Swine flu studies. They racked up a lot of citations this year. (You may not be too surprised.)

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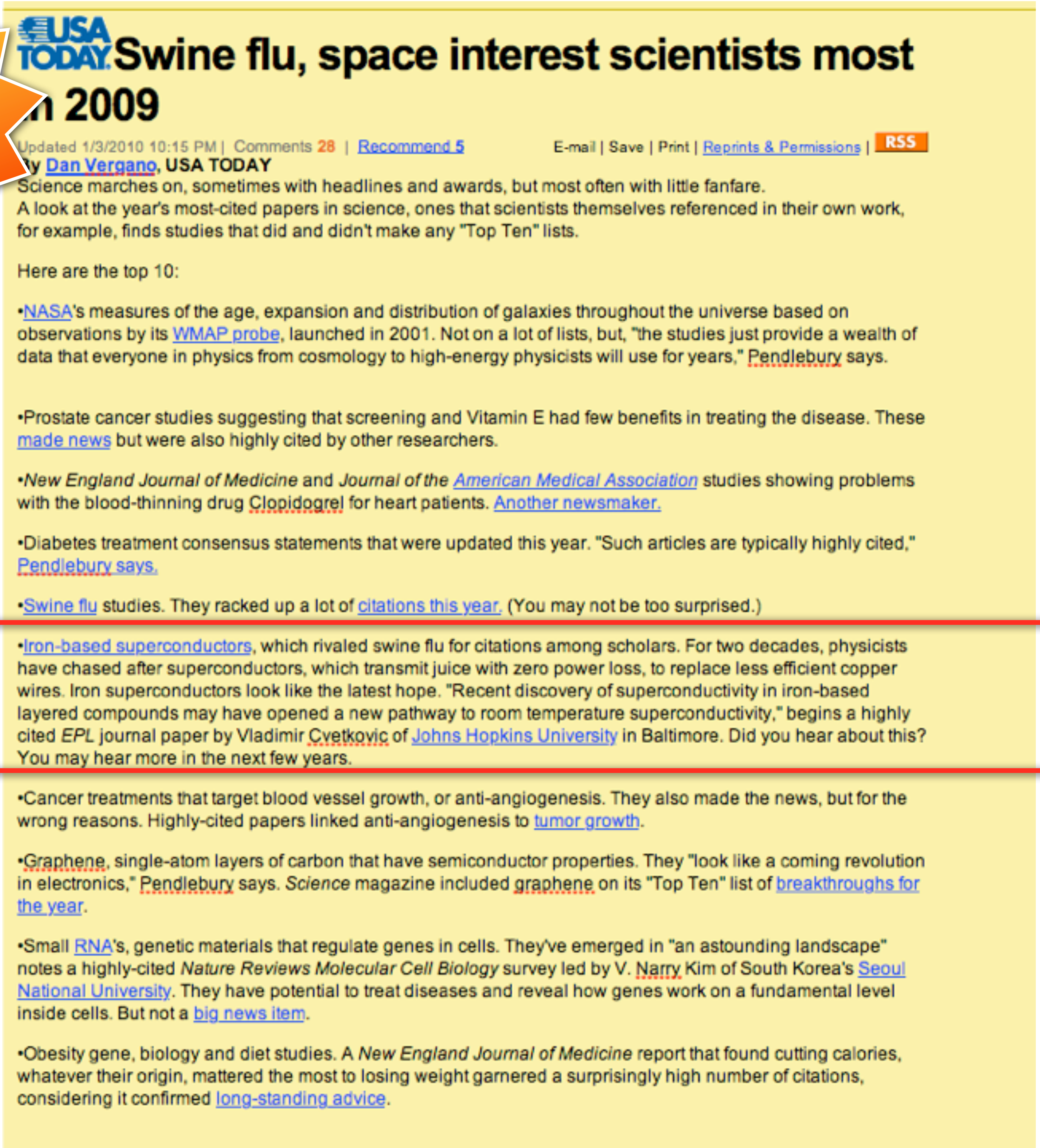
Top Ten
most cited articles
in 2009



Swine flu, space interest scientists most n 2009

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y Dan Vergano, USA TODAY

Science marches on, sometimes with headlines and awards, but most often with little fanfare.
A look at the year's most-cited papers in science, ones that scientists themselves referenced in their own work, for example, finds studies that did and didn't make any "Top Ten" lists.

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Fe-based
Supercon-
ductors
rivaled
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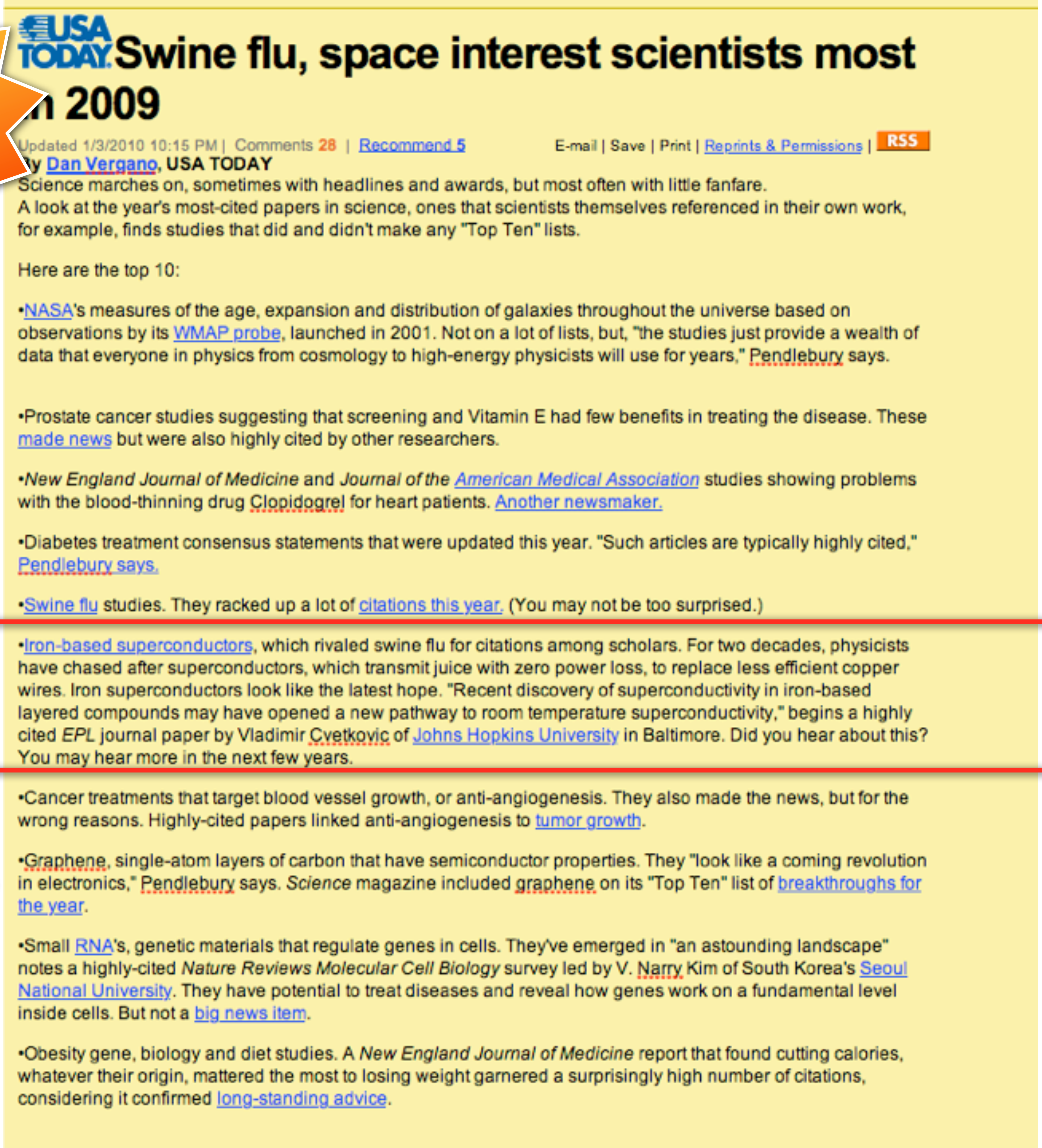

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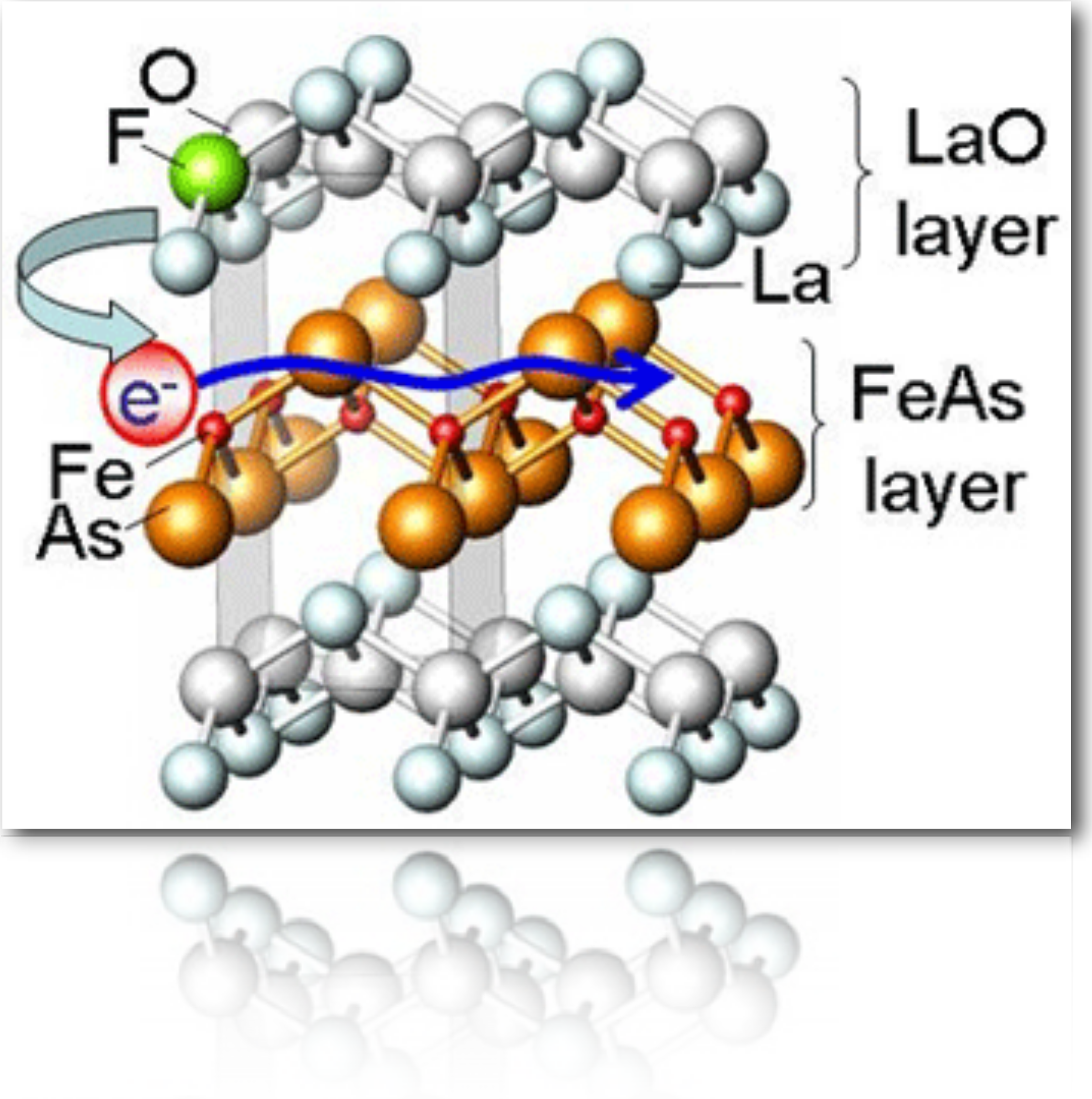
Fe-based Supercon-ductors rivaled Swine flu

Crystal Structure of $LaFeAsO_{1-x}F_x$

Tetragonal

Space group : *P4/nmm*



Dopant Layer

Conduction Layer

Lattice constants

$a = 4.035$ Å

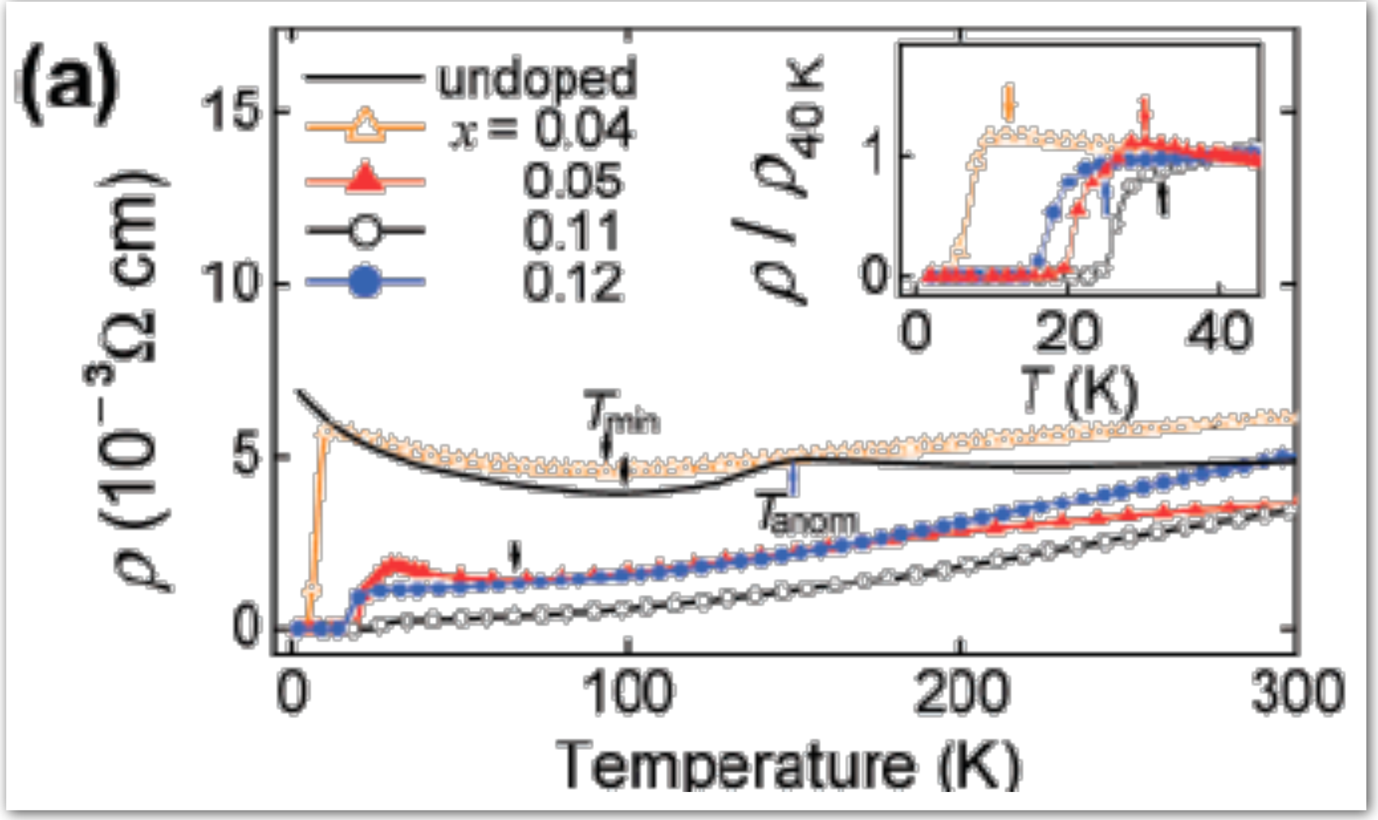
$c = 8.740$ Å

Two formula units per unit cell

Alternate stacking of $(R_2O_2)^{2+}$ and $(Fe_2As_2)^{2-}$ layers

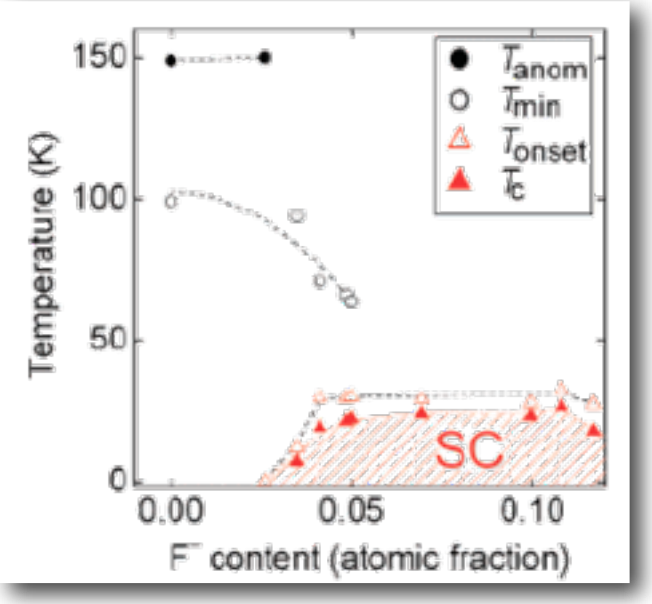
Electrical Resistivity

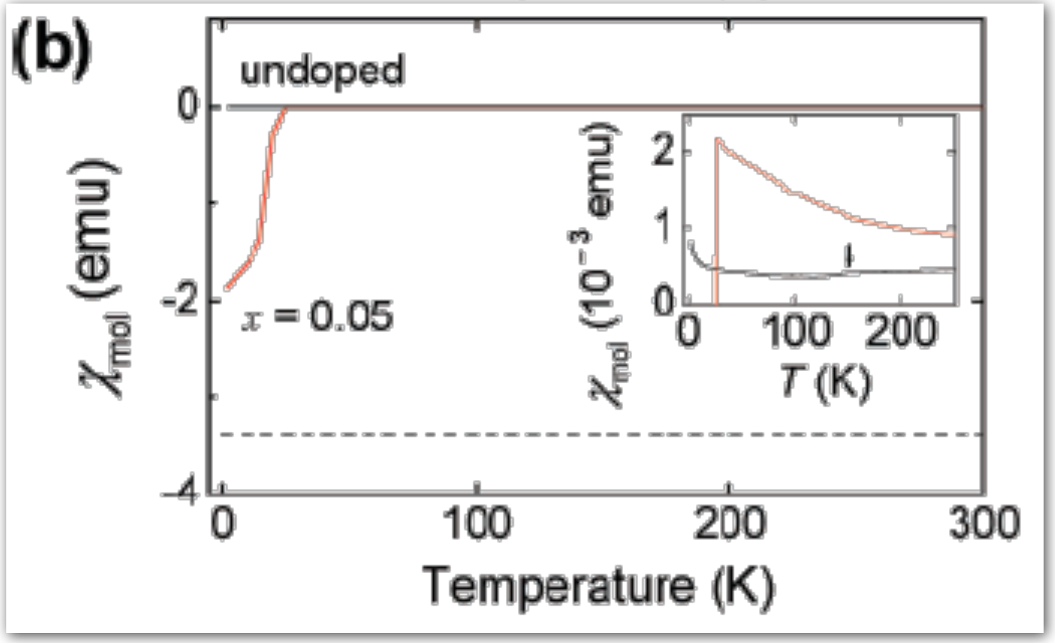
$LaFeAsO_{1-x}F_x$



J. Am. Chem. Soc. 130 (2008) 3296

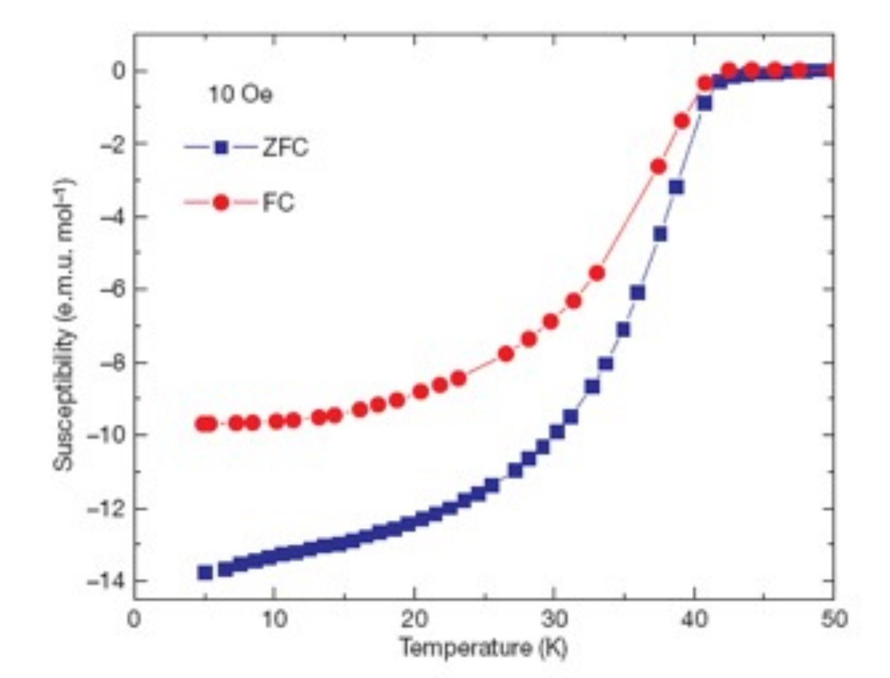
Tc max ≈ 26 K for x = 0.11

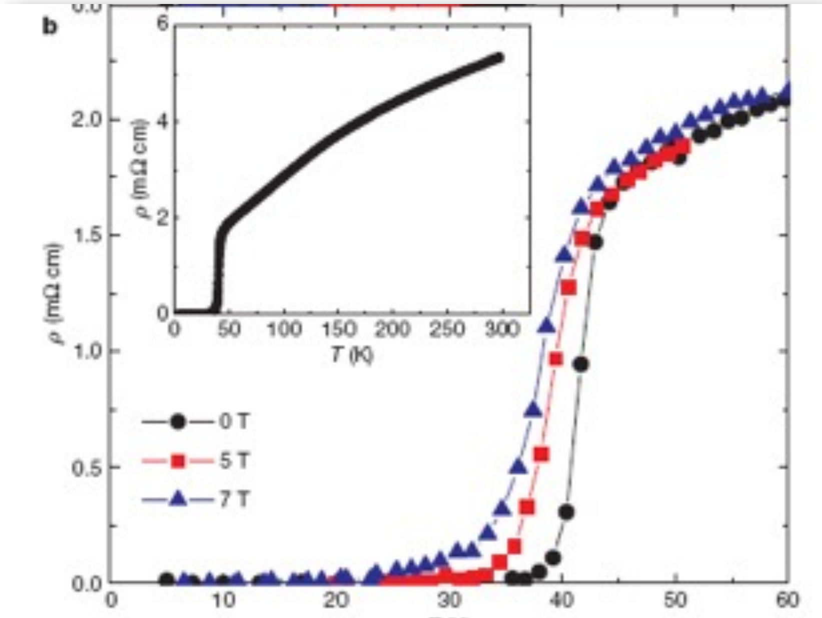


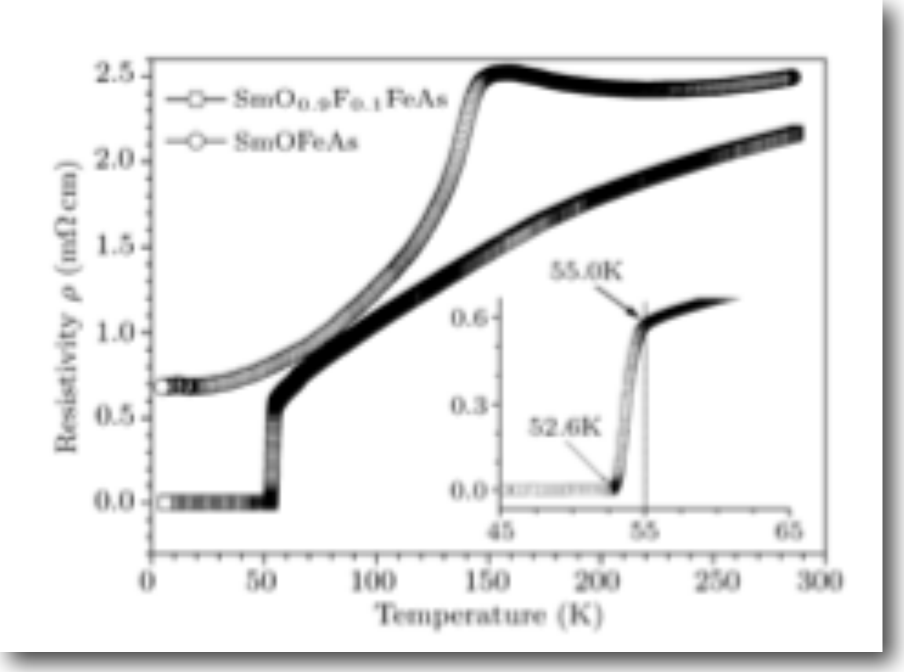


$SmFeAsO_{1-x}F_x$

Superconductivity at 43 K.
Chen et al , Nature 453 (2008) 761.







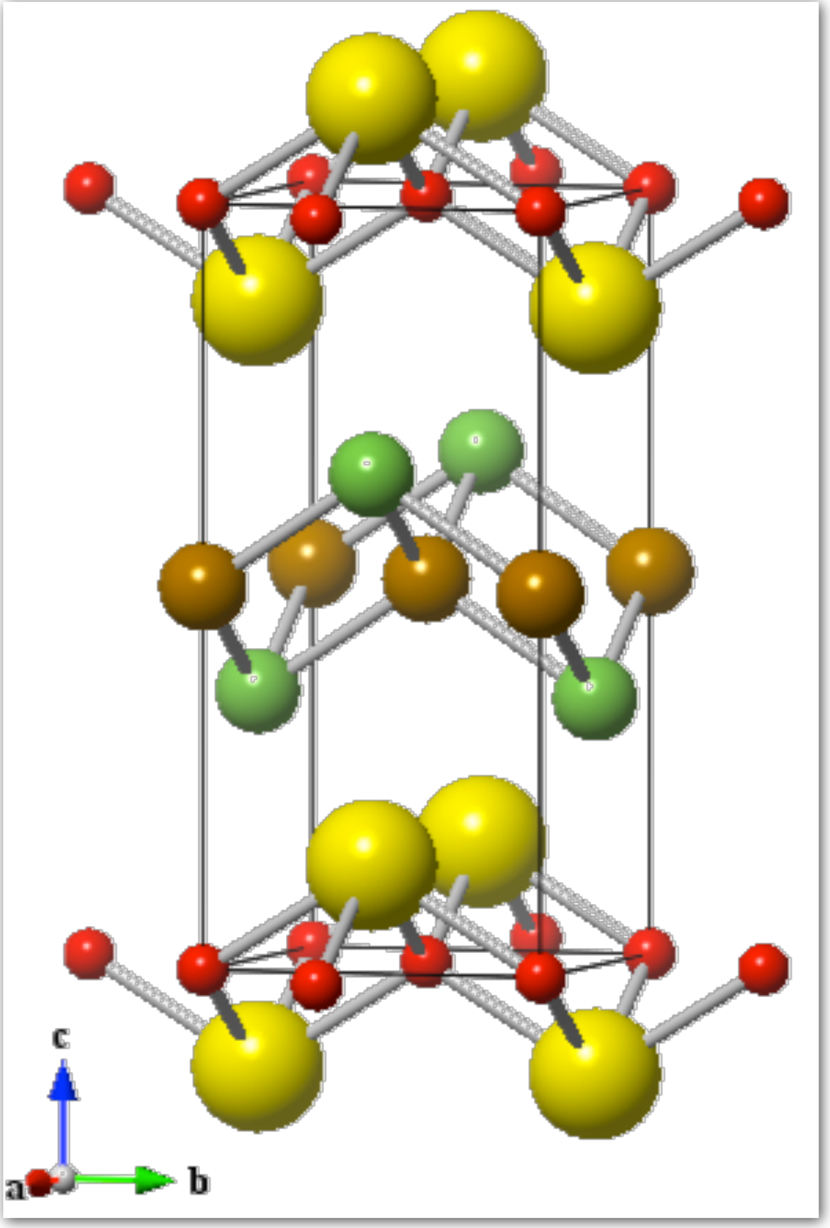
Highest Tc 55 K

$(RE)FeAsO_{1-x}F_x$ where RE = Ce, Pr, Nd, Sm, Gd and Tb also showed superconducting transitions close to 50 K.

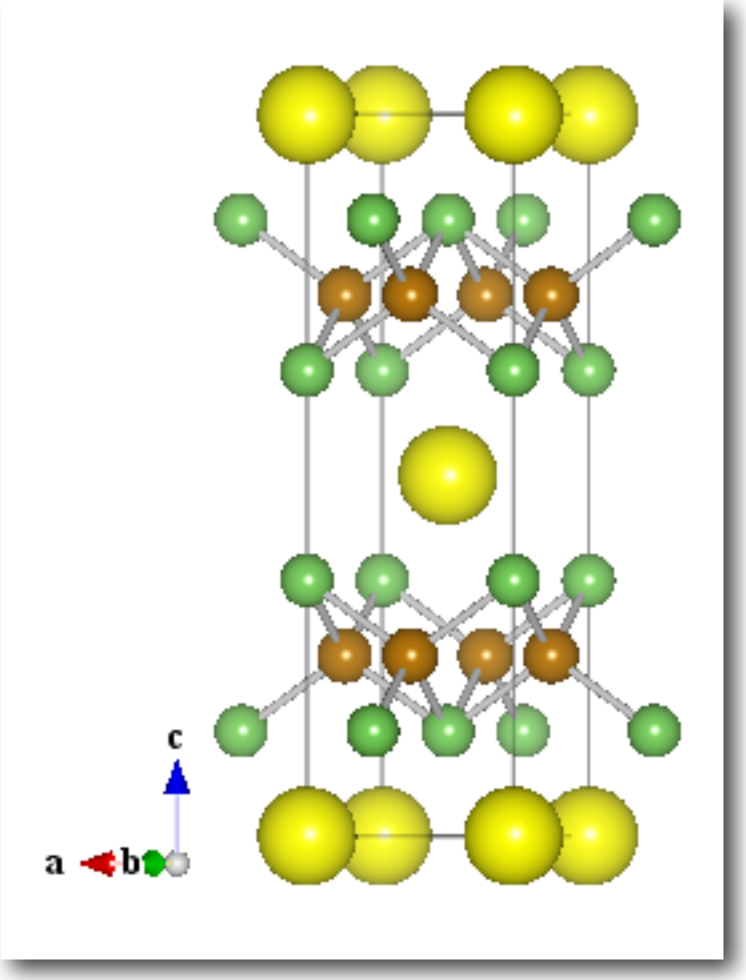
AFe_2As_2 (A = Ba, Sr, Ca and Eu)

Structural similarity

LaFeAsO



AFe_2As_2

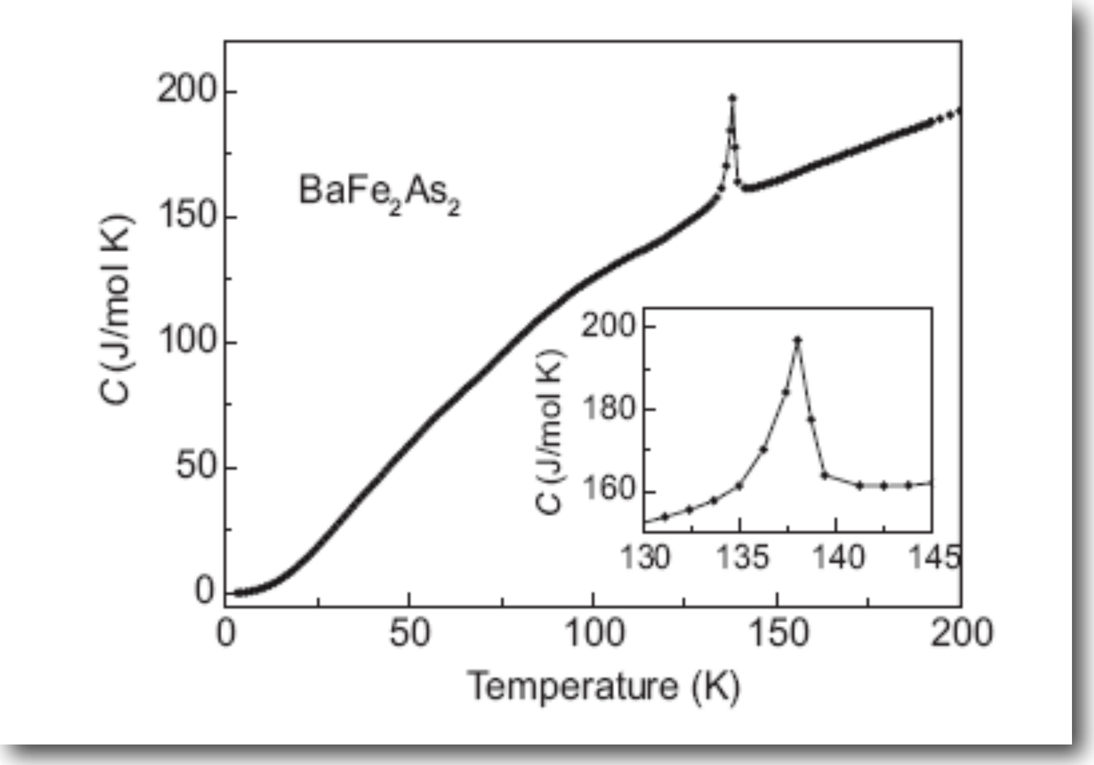


Exchanging $(R_2O_2)^+$ layer with a single large *A* atom leads to $ThCr_2Si_2$ type structure

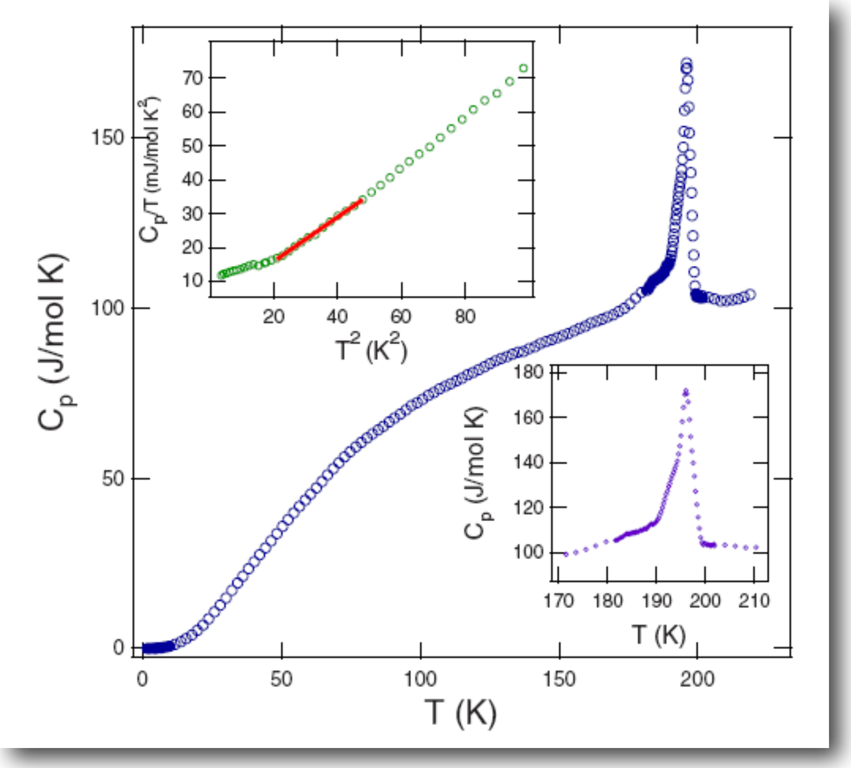
To keep the electron count *A* has to be divalent

Heat capacity of AFe_2As_2 (A = Ba, Sr, Ca and Eu)

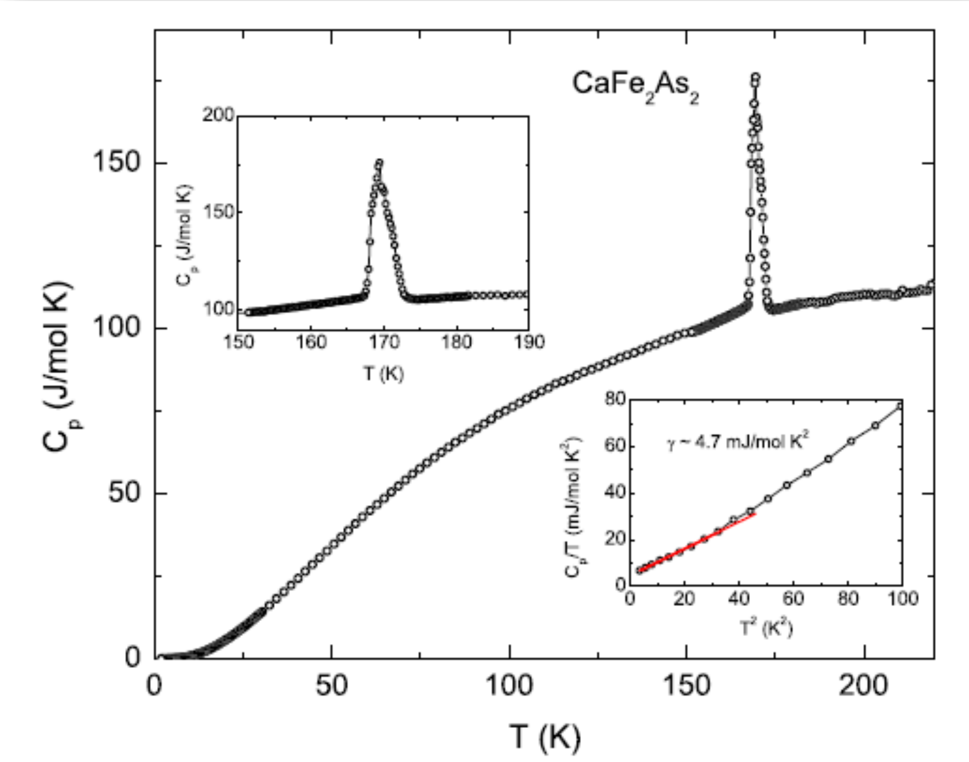
$BaFe_2As_2$ T_{SDW} = 137 K



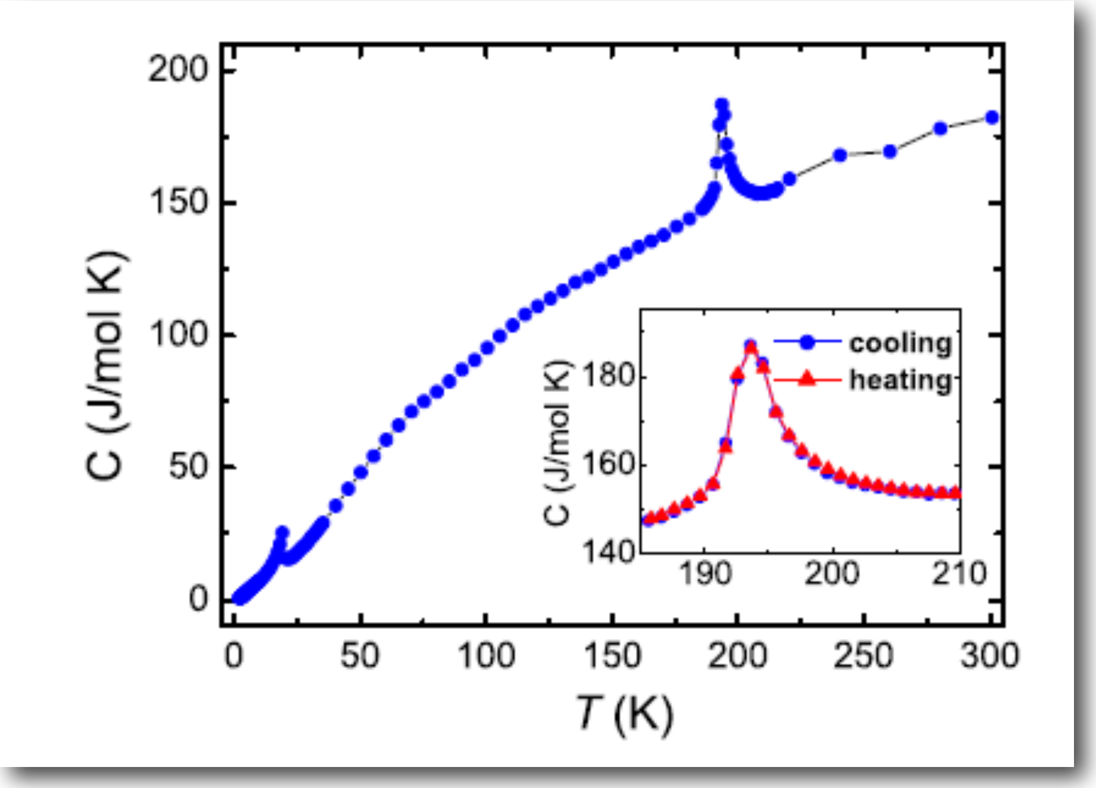
$SrFe_2As_2$ T_{SDW} = 198 K



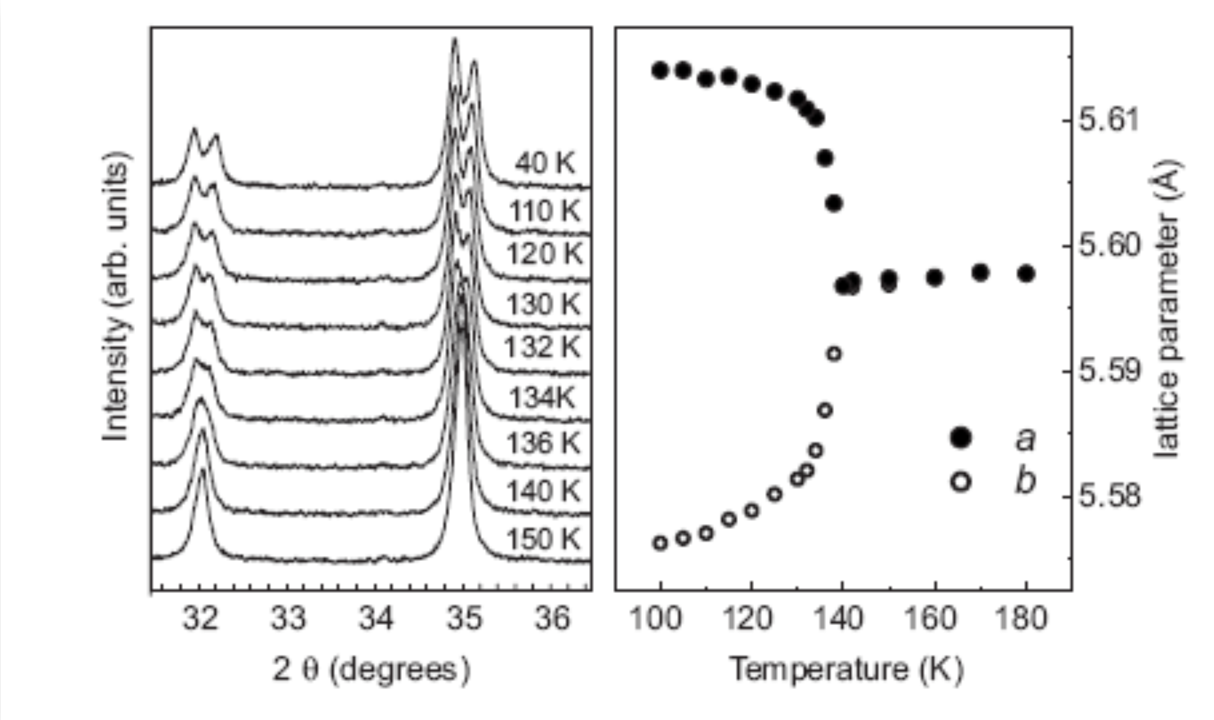
$CaFe_2As_2$ T_{SDW} = 170 K



$EuFe_2As_2$ T_{SDW} = 195 K; T_N = 19 K



X-ray diffraction of $BaFe_2As_2$



Splitting of (110) and (112) reflections

M Rotter Phys. Rev. B 78 (2008) 020503

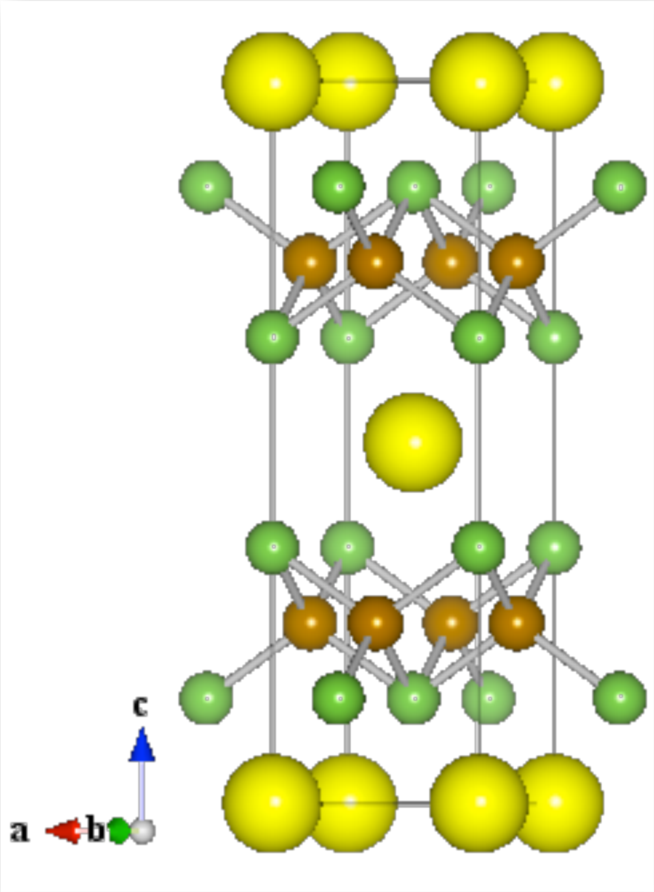
300 K

Tetragonal

I4/mmm

$a = 3.962$ Å

$c = 13.0168$ Å



20 K

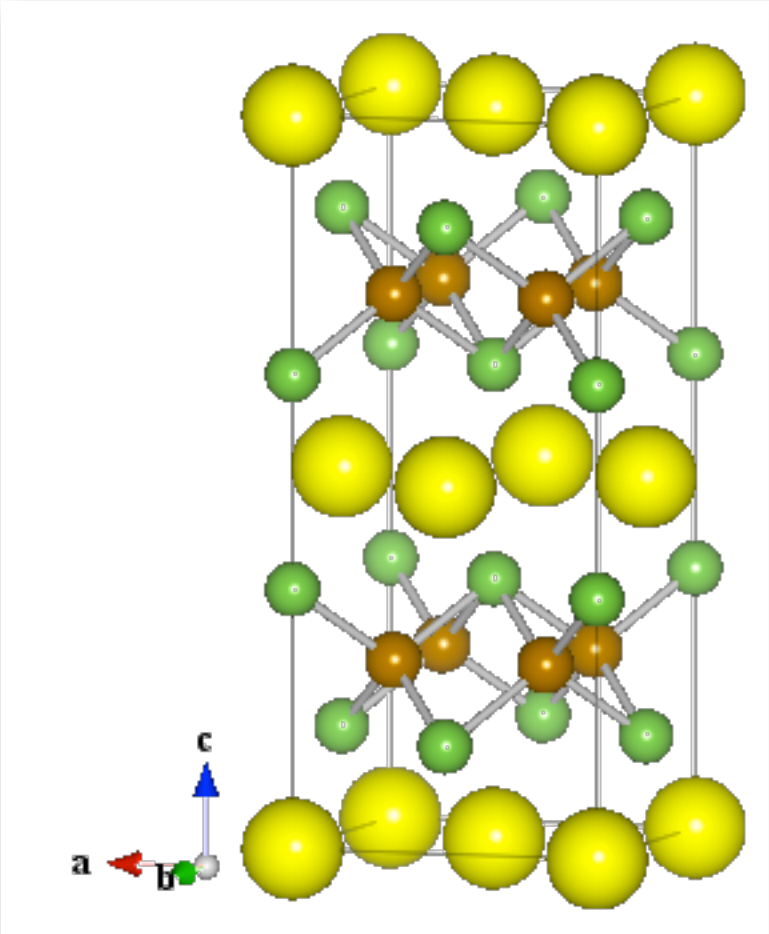
Orthorhombic

Fmmm

$a = 5.614$ Å

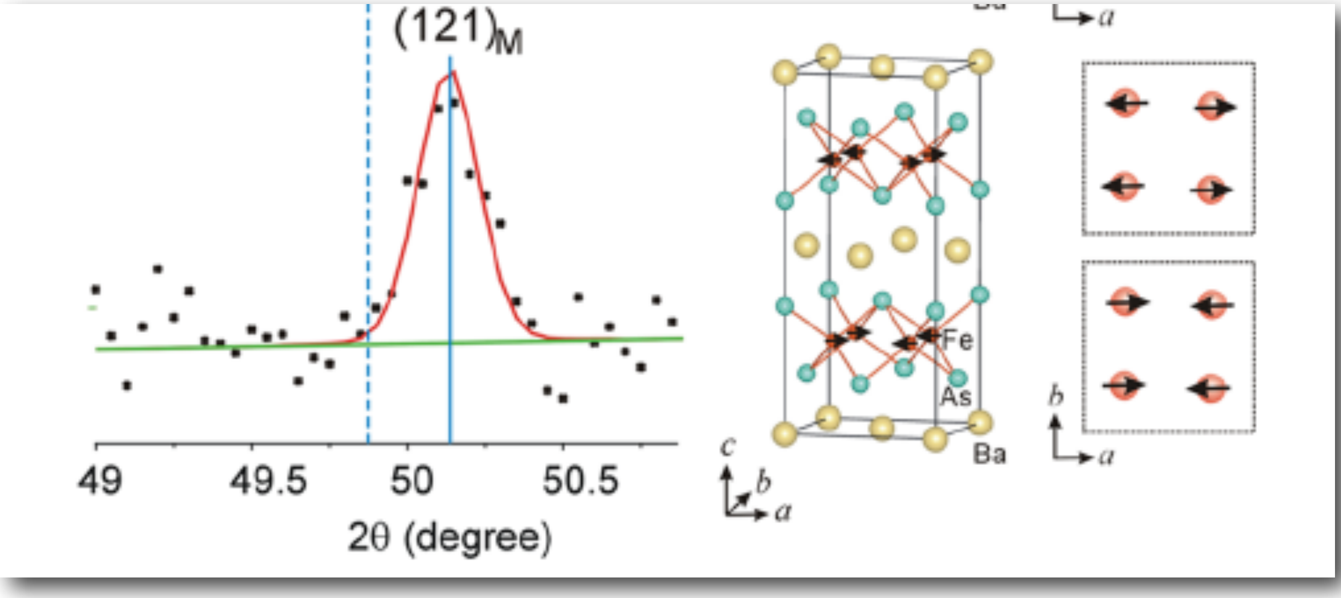
$b = 5.574$ Å

$c = 12.940$ Å



Neutron diffraction studies of AFe_2As_2

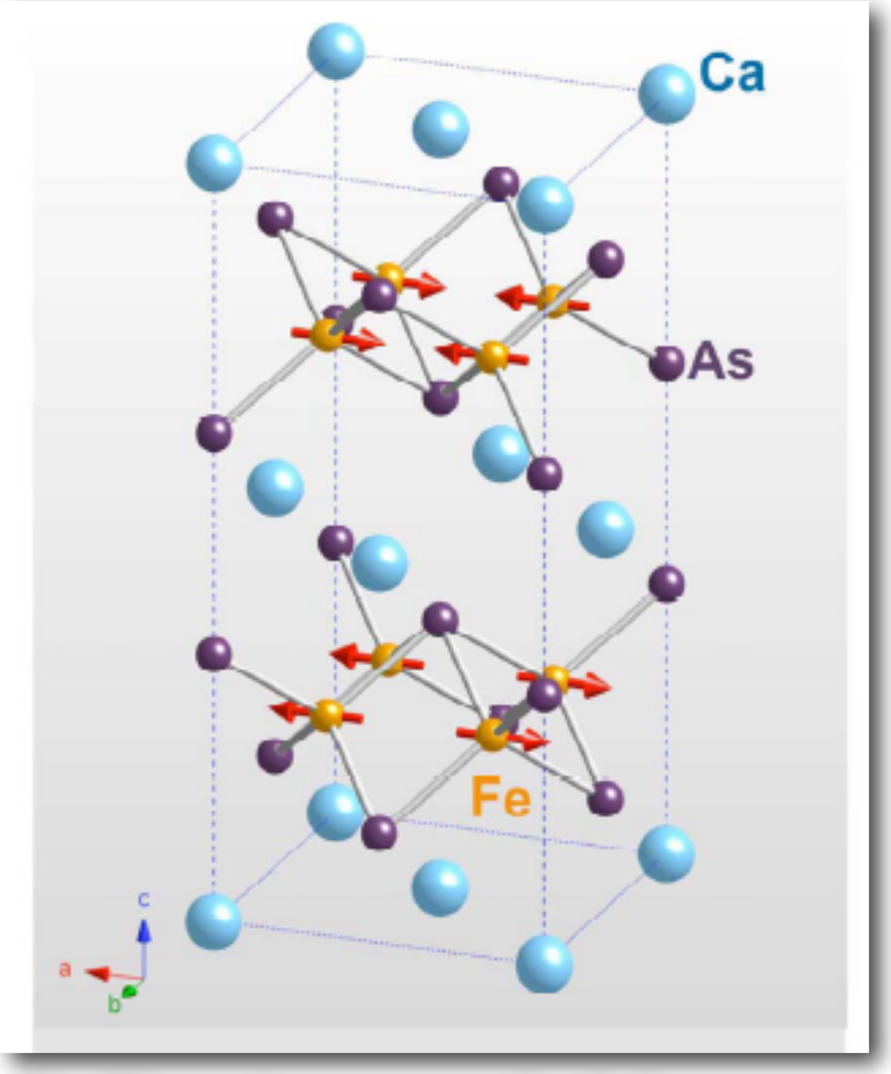
$BaFe_2As_2$



0.87 μB

Below the magnetic ordering in the orthorhombic phase

Fe orders AF along *a* and *c* axes and Ferromagnetically along *b*-axis

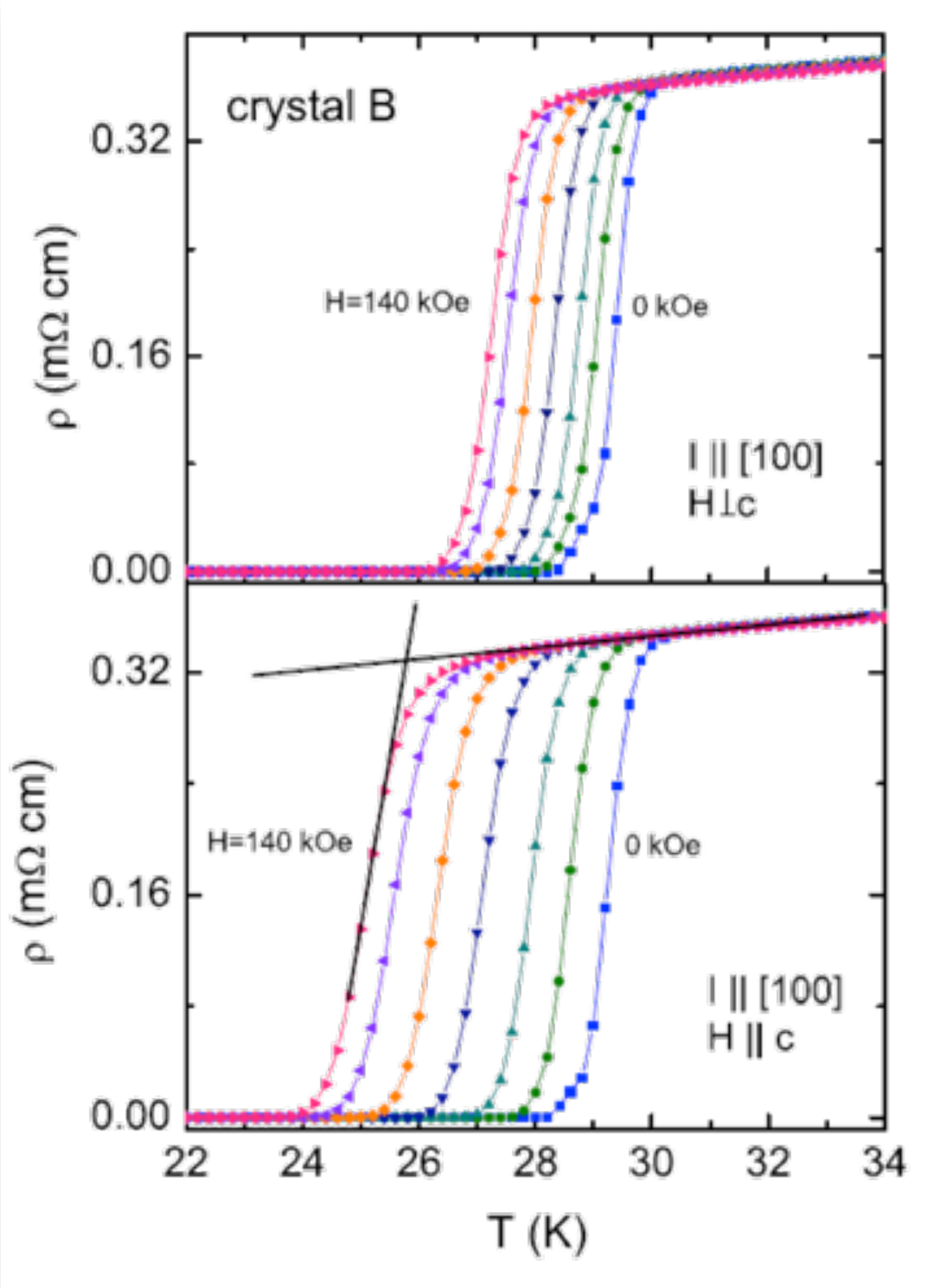


$CaFe_2As_2$ 0.80 μB

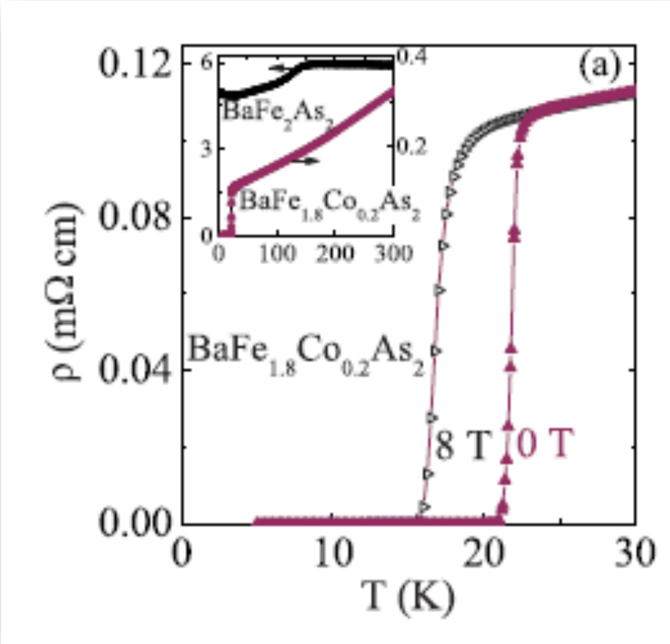
Superconductivity AFe_2As_2

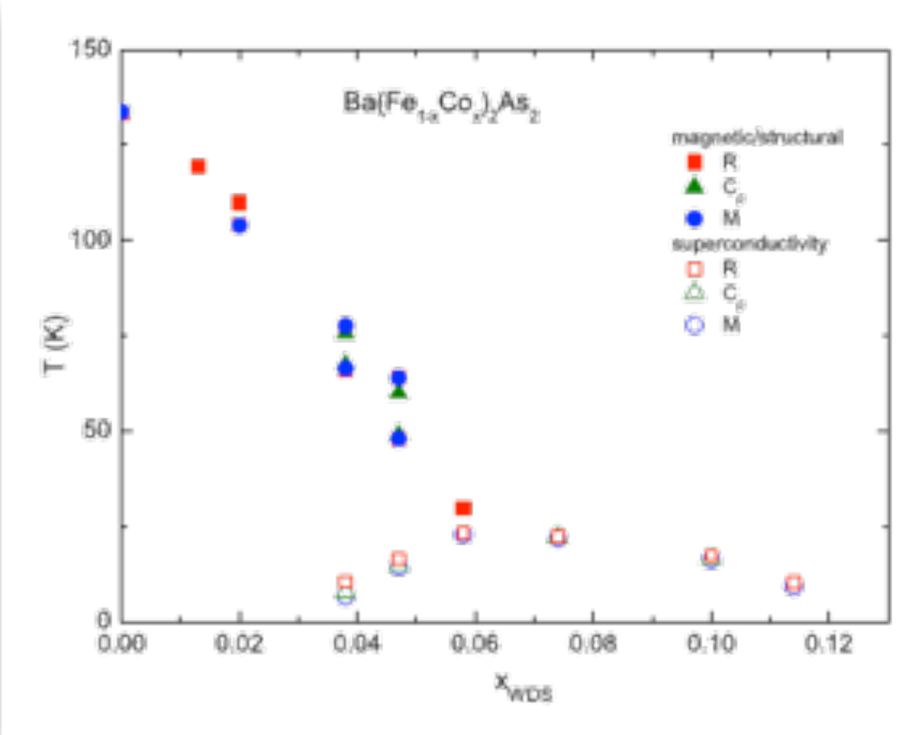
All of the AFe_2As_2 compounds exhibit superconductivity either by doping or by applying pressure

$Ba_{1-x}K_xFe_2As_2$ Tc = 30 K

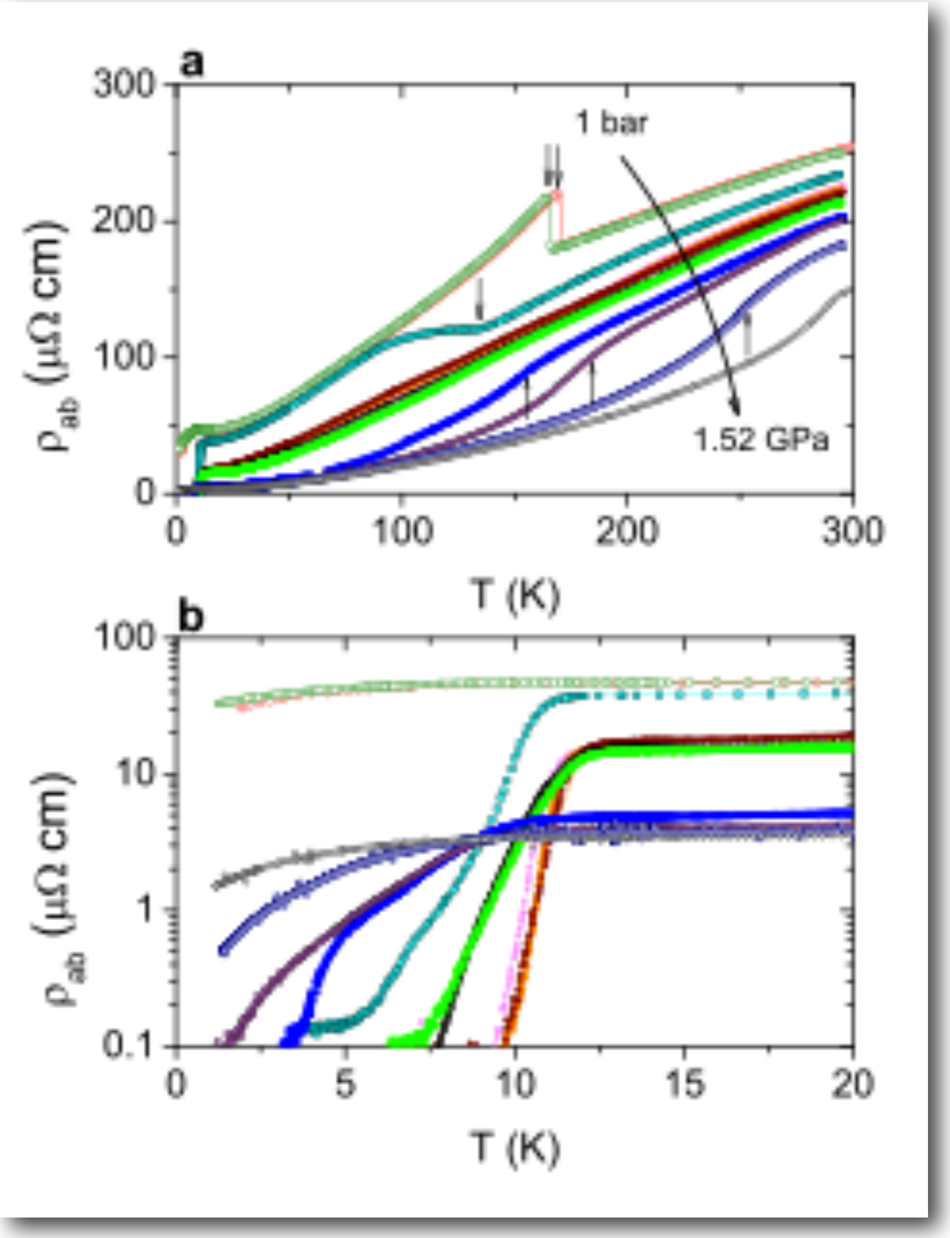


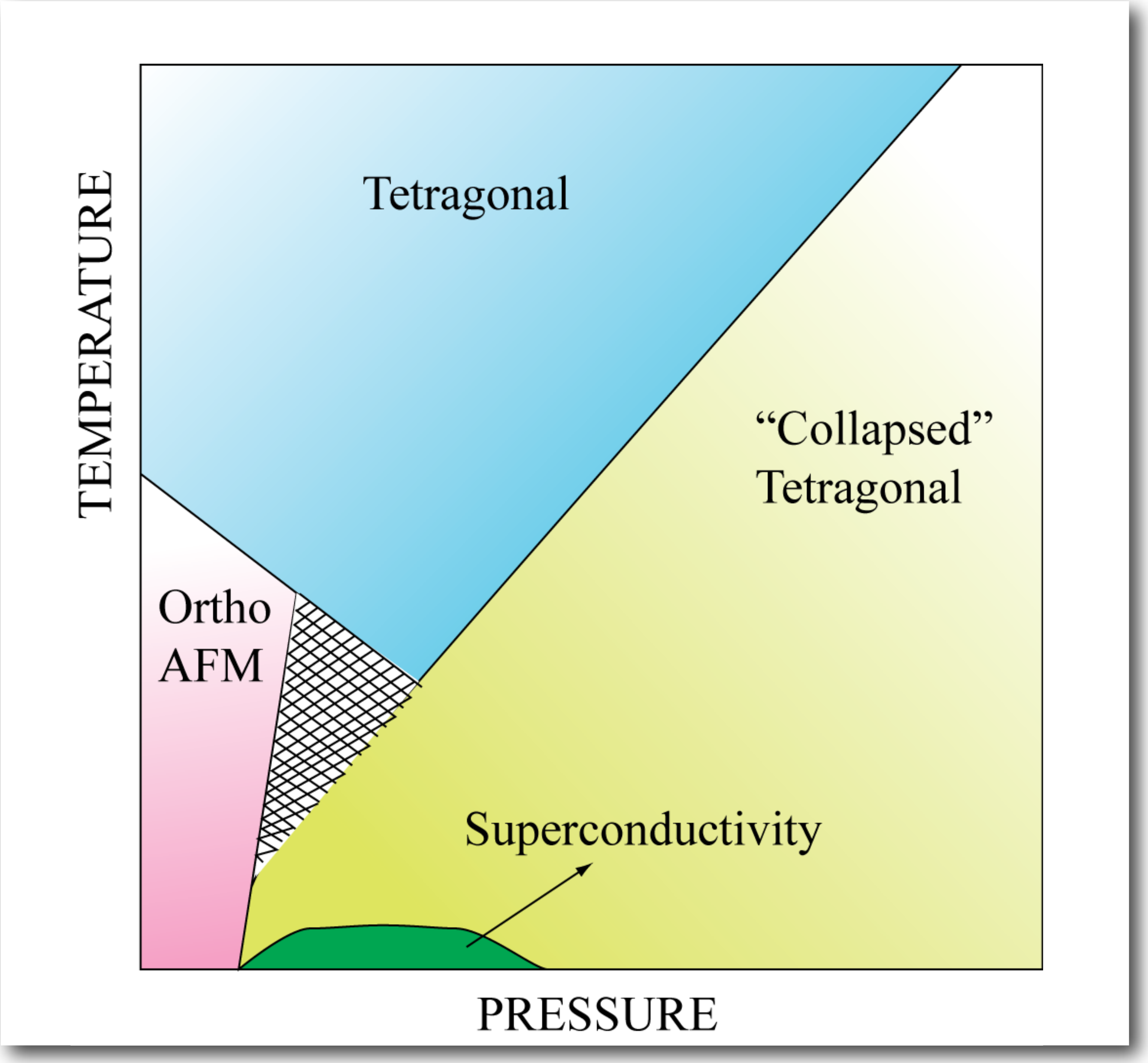
$BaFe_{2-x}Co_xAs_2$ Tc = 22 K





Pressure induced superconductivity $CaFe_2As_2$



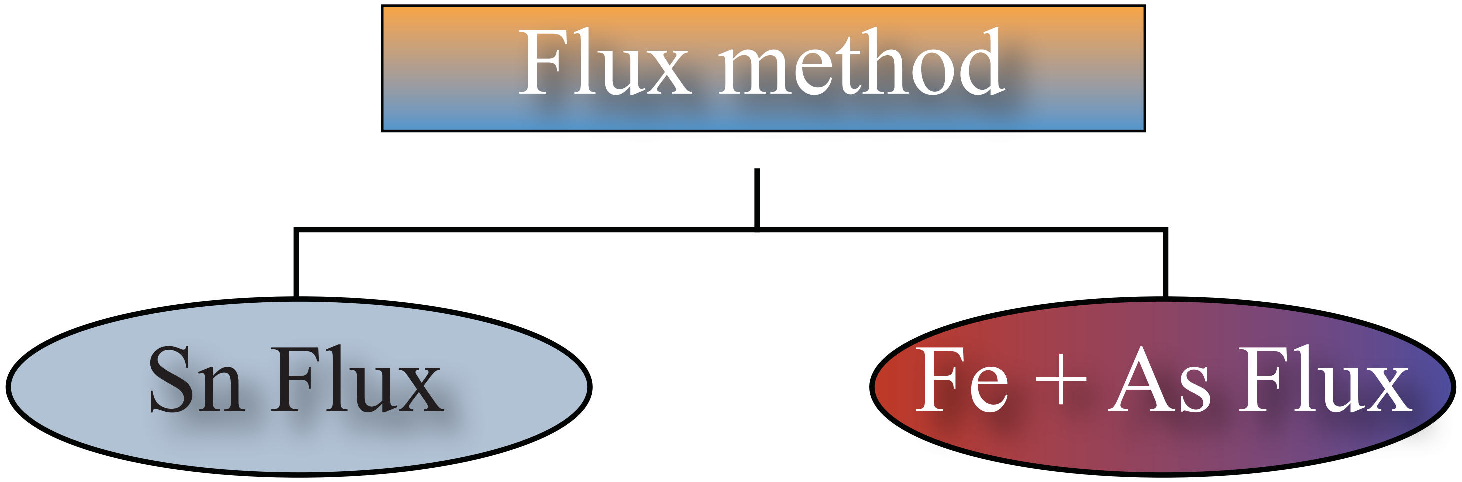


A. Kreyssig *et al* Phys. Rev B 78 (2008) 184517

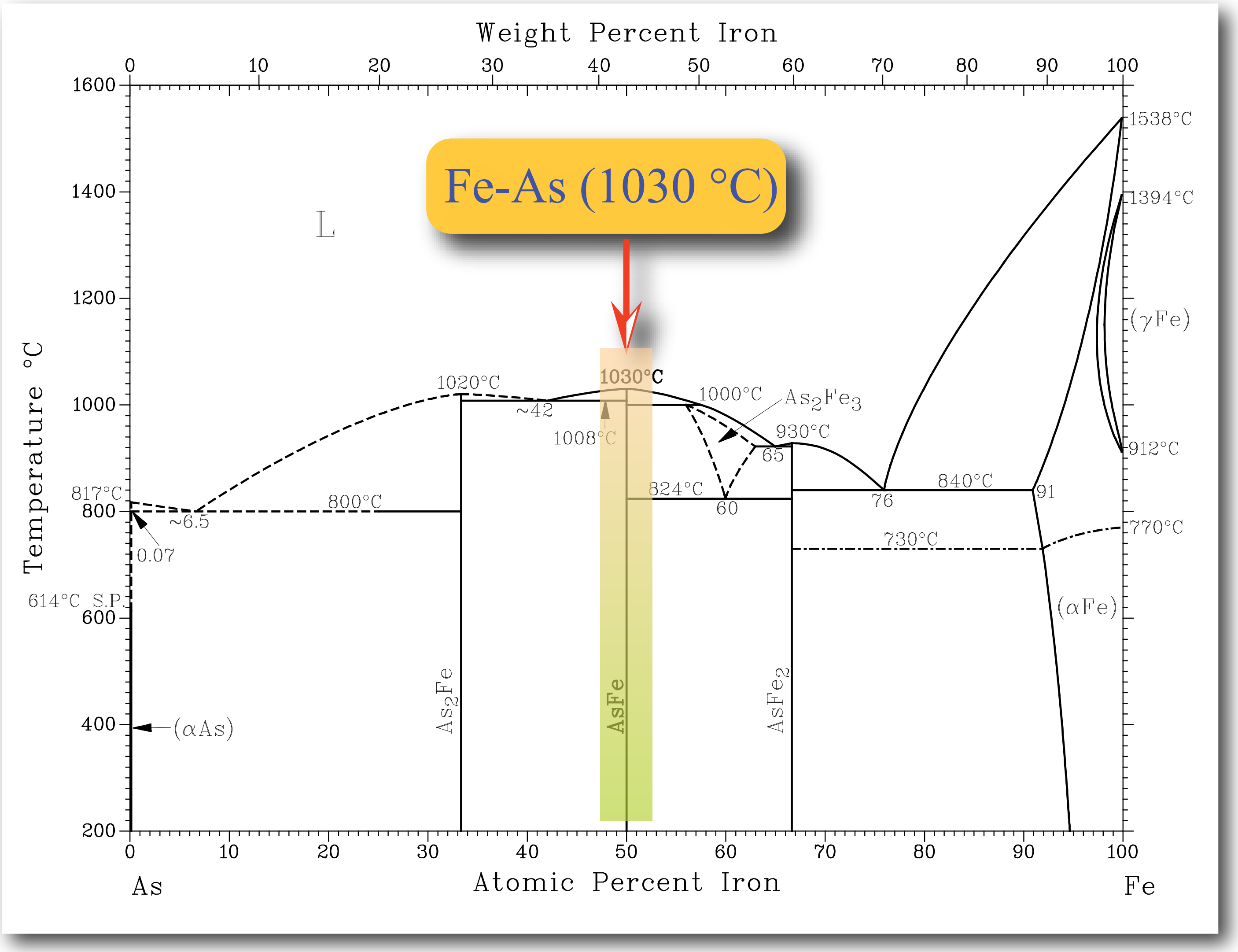
Magnetically ordered Orthorhombic phase - Non magnetically ordered collapsed tetragonal phase

Pressure induced superconductivity appears in the collapsed tetragonal phase

Crystal growth of AFe_2As_2



Binary Phase diagram of Fe-As

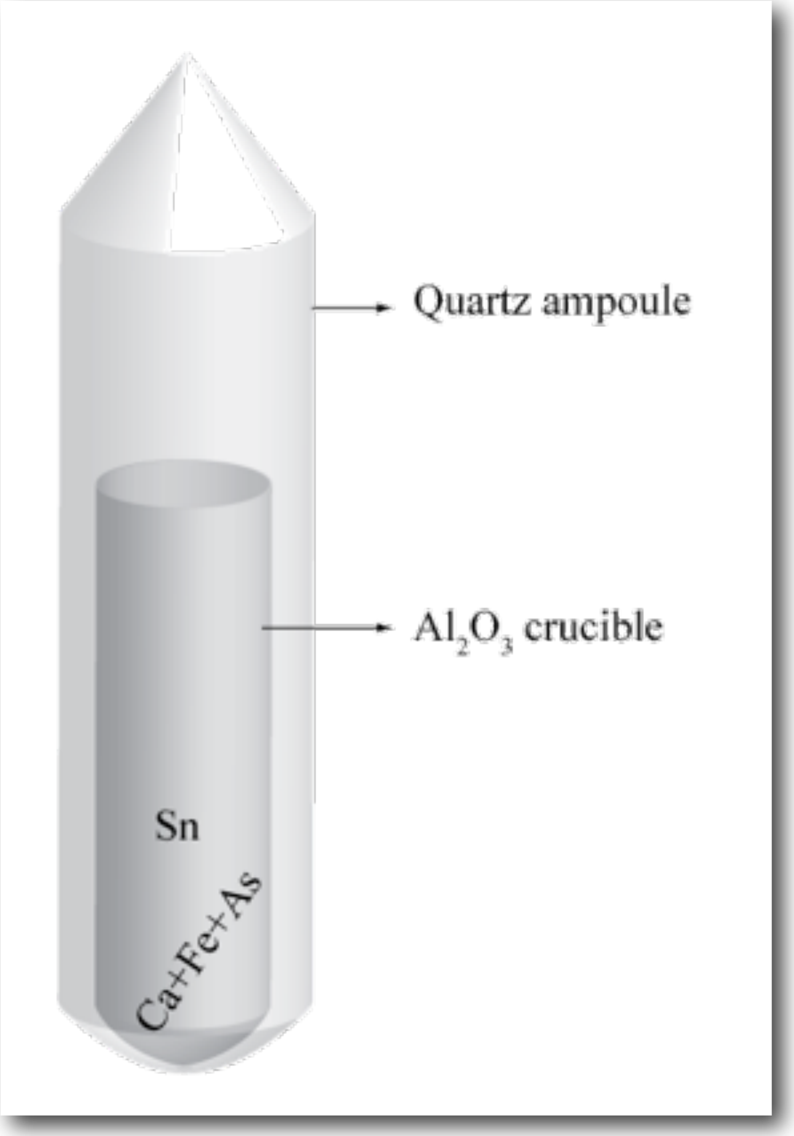


Fe-As (1030 °C)

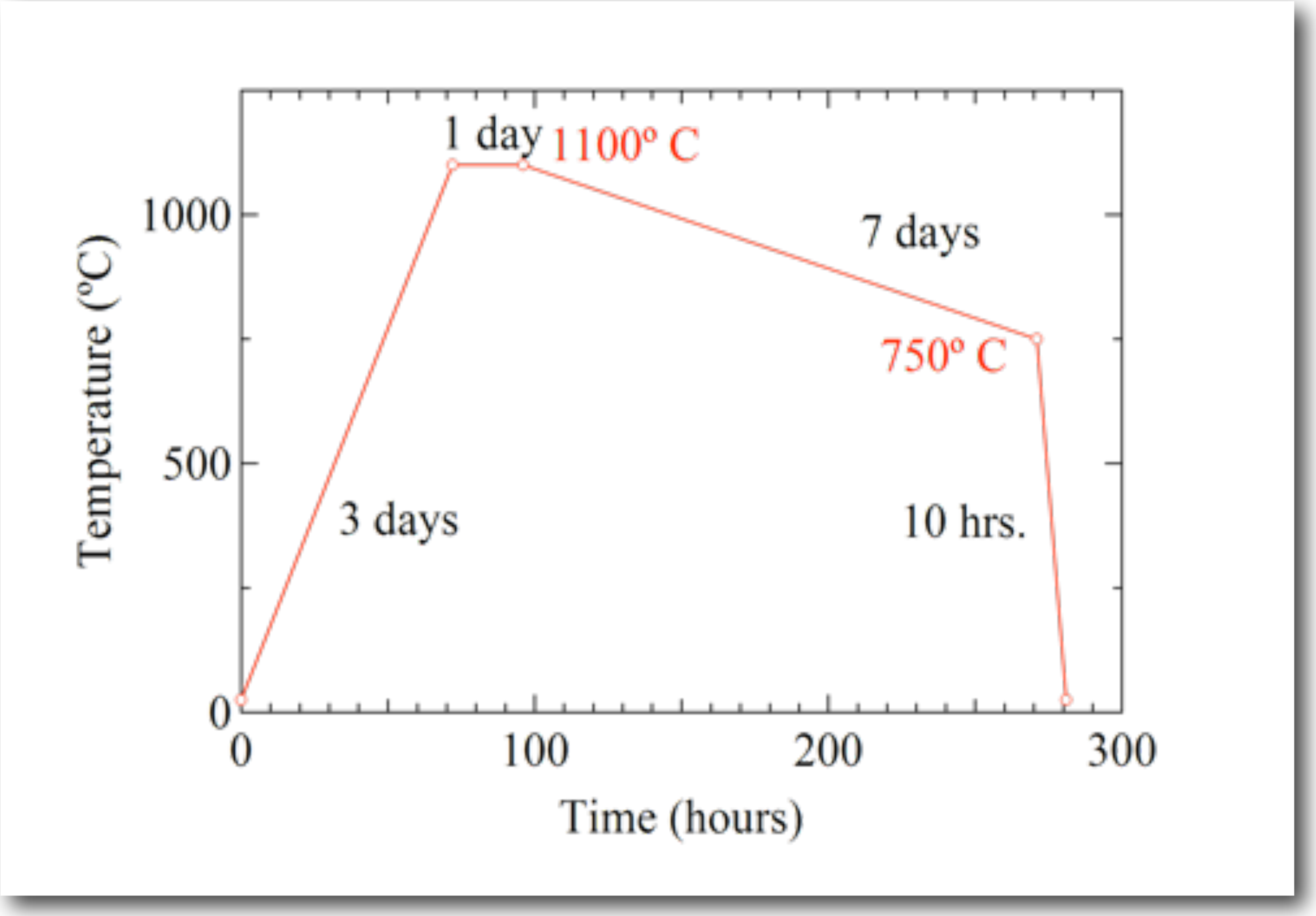
Crystal growth of AFe_2As_2 (A = Ca, Sr, Ba and Eu)

Using Sn as flux

A	Fe	As	Sn
1	2	2	19

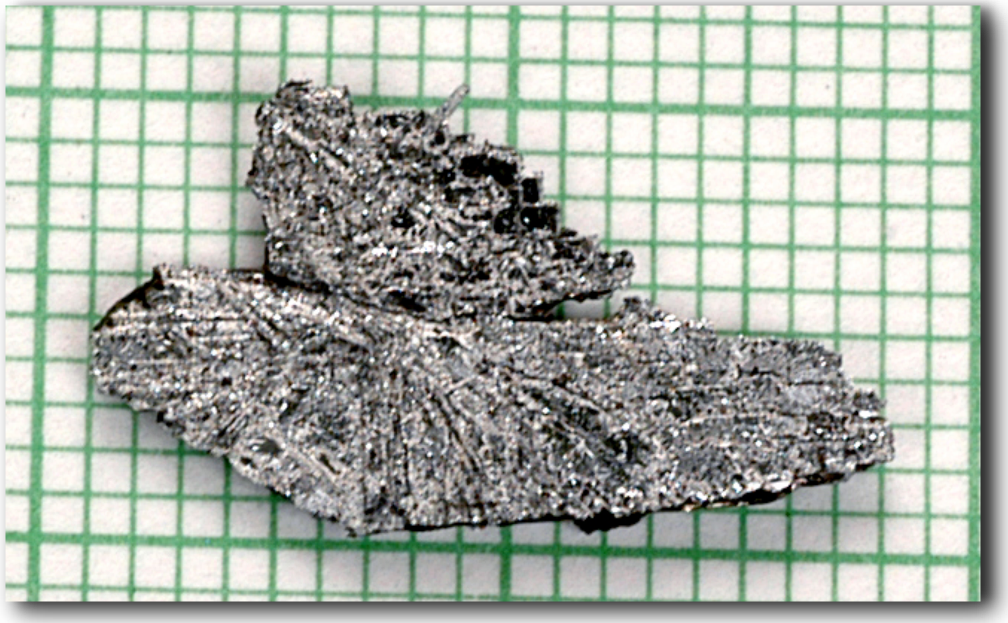


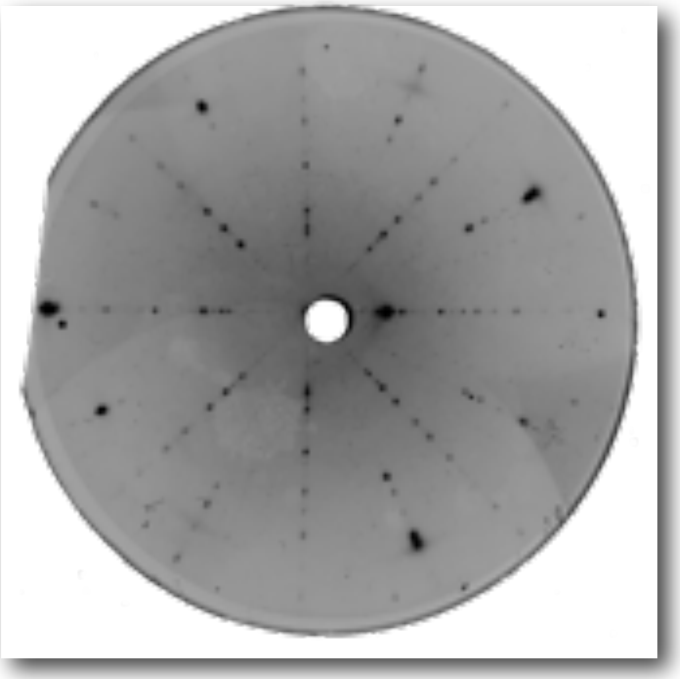
Temperature Profile



As grown single crystals

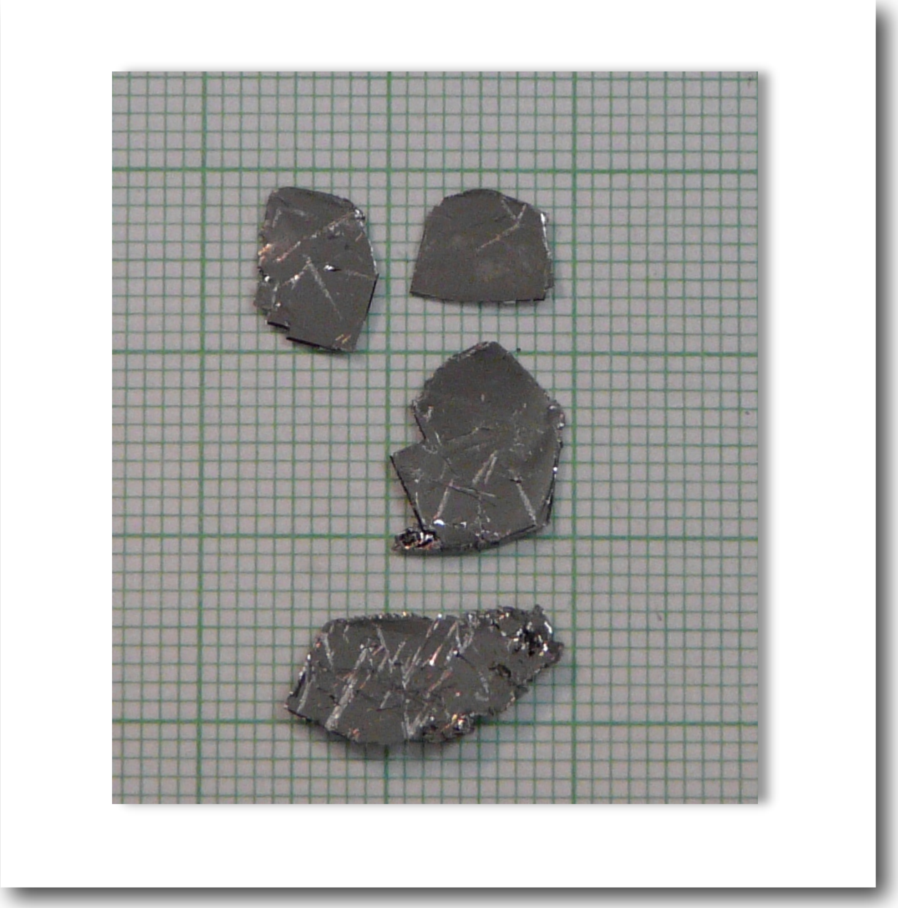
$CaFe_4As_3$ needle like crystals on the surface



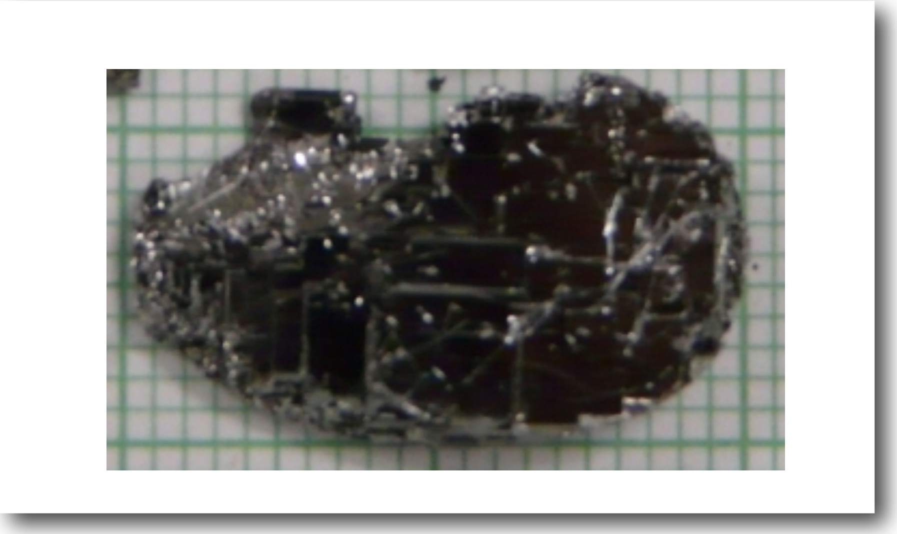


The flat plane (001)

$CaFe_2As_2$ crystals

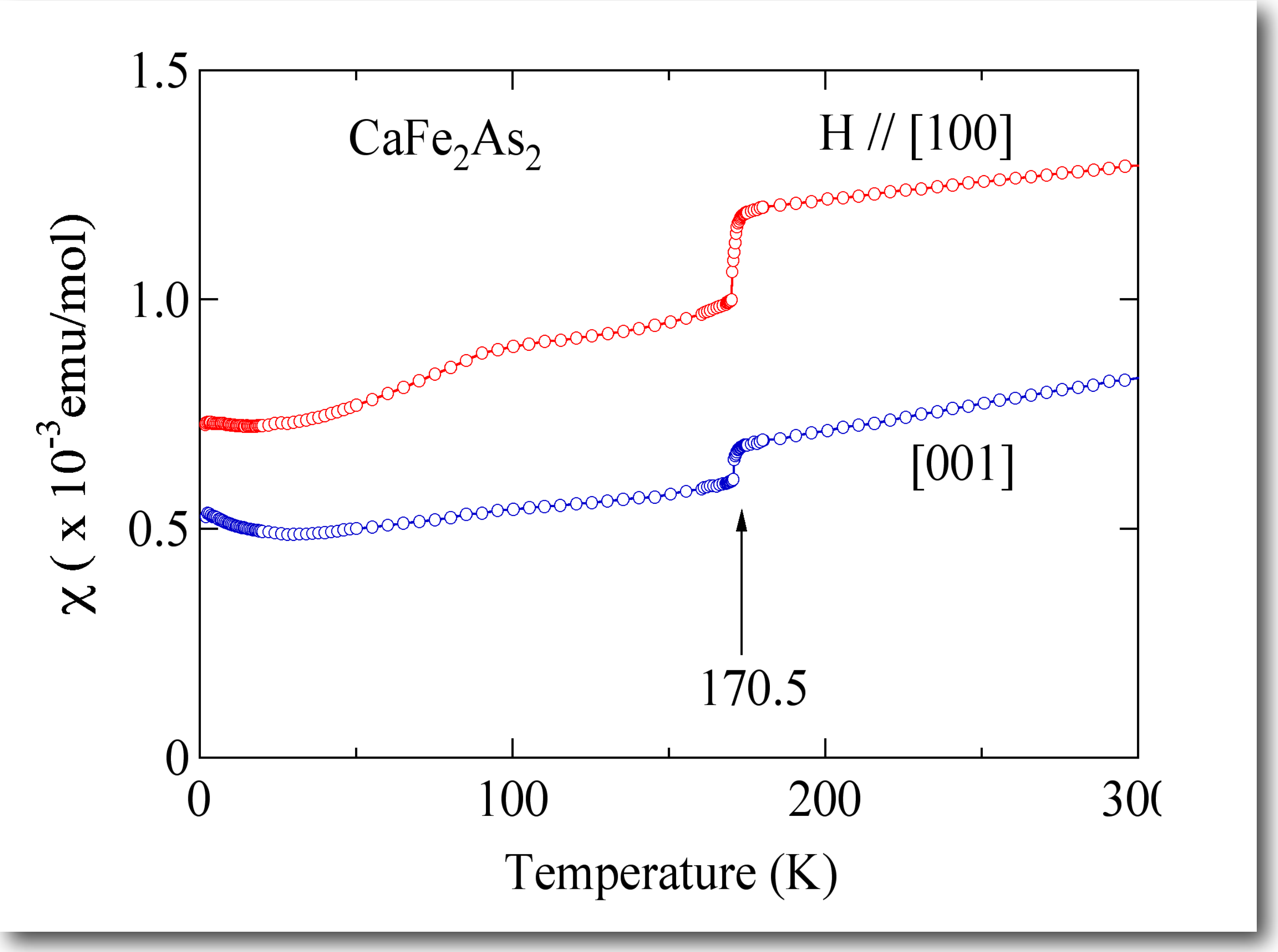


$SrFe_2As_2$ crystal



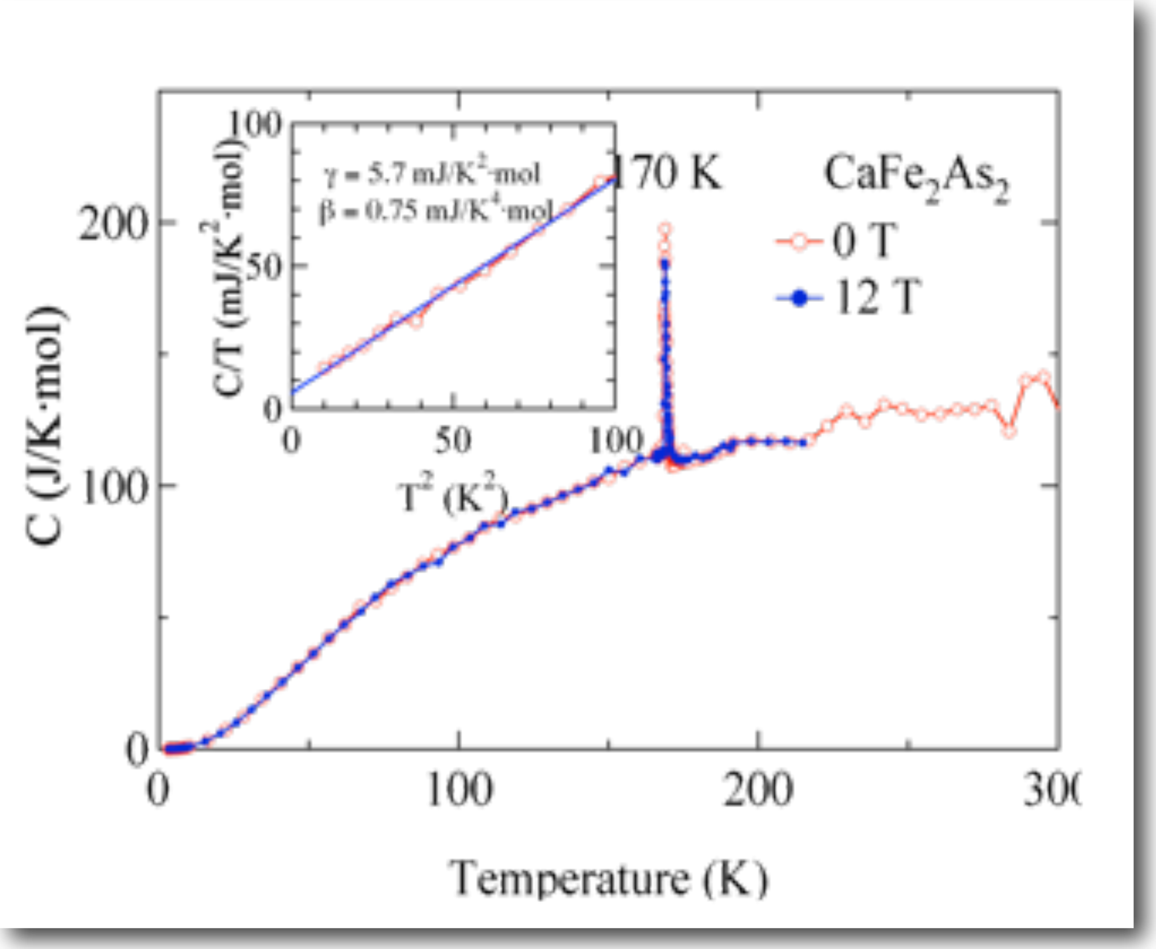
$CaFe_2As_2$

Magnetic Susceptibility

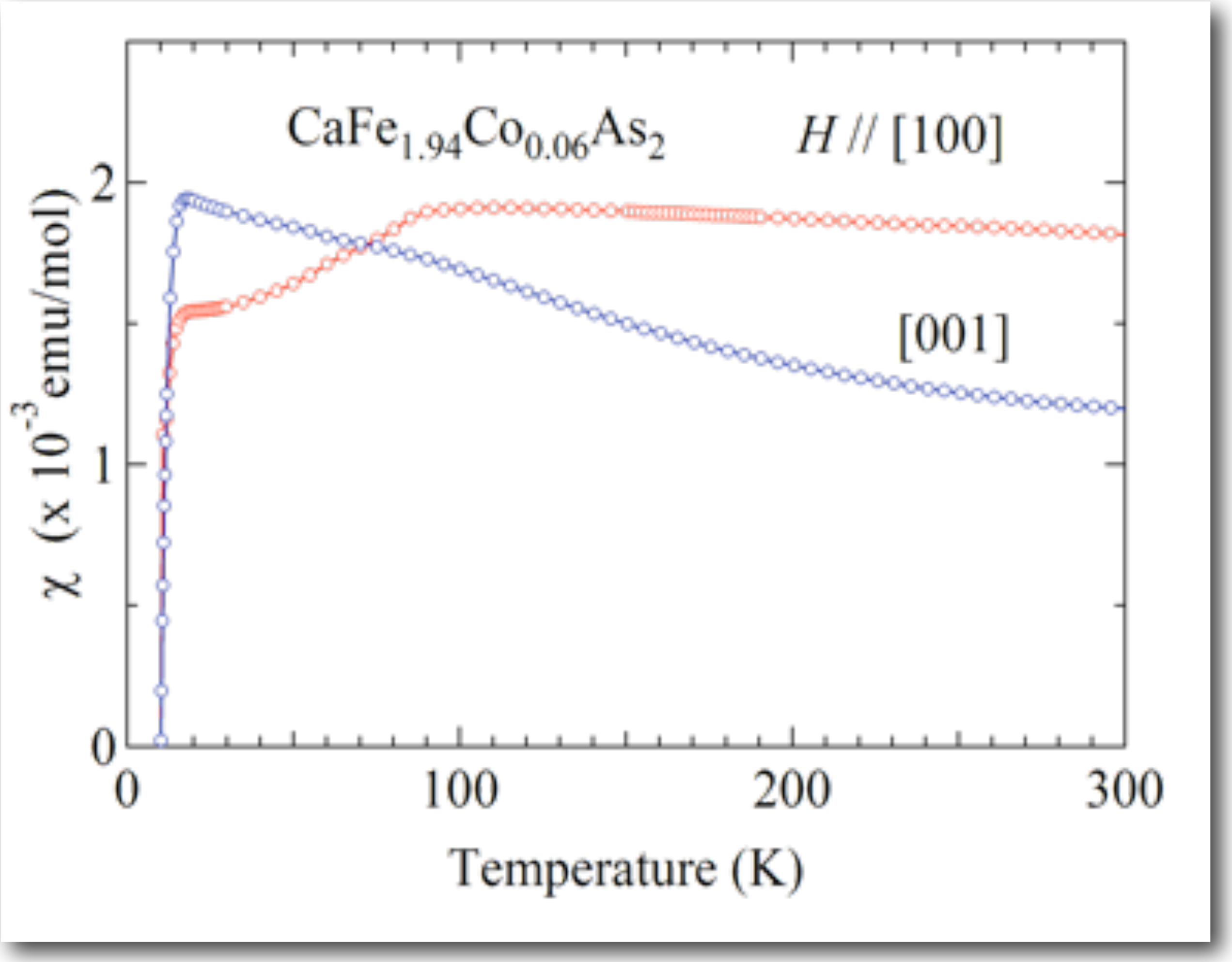


170 K

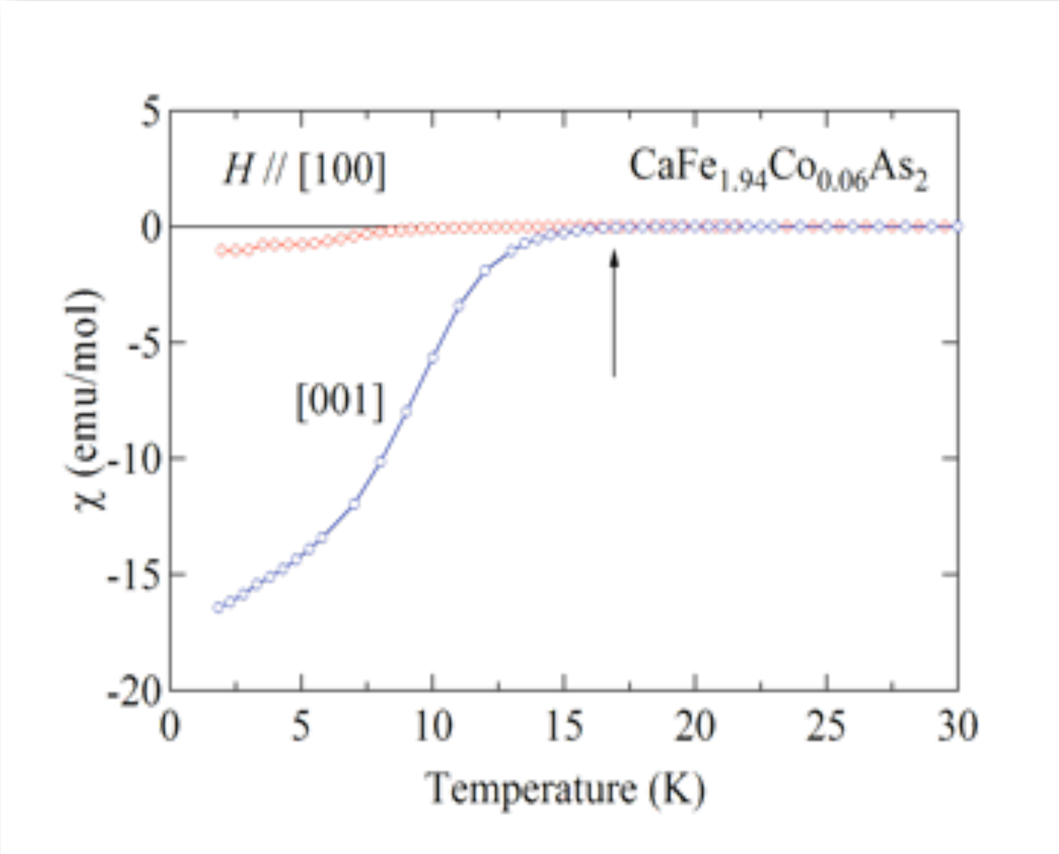
Structural / Magnetic transition



$CaFe_{1.94}Co_{0.06}As_2$

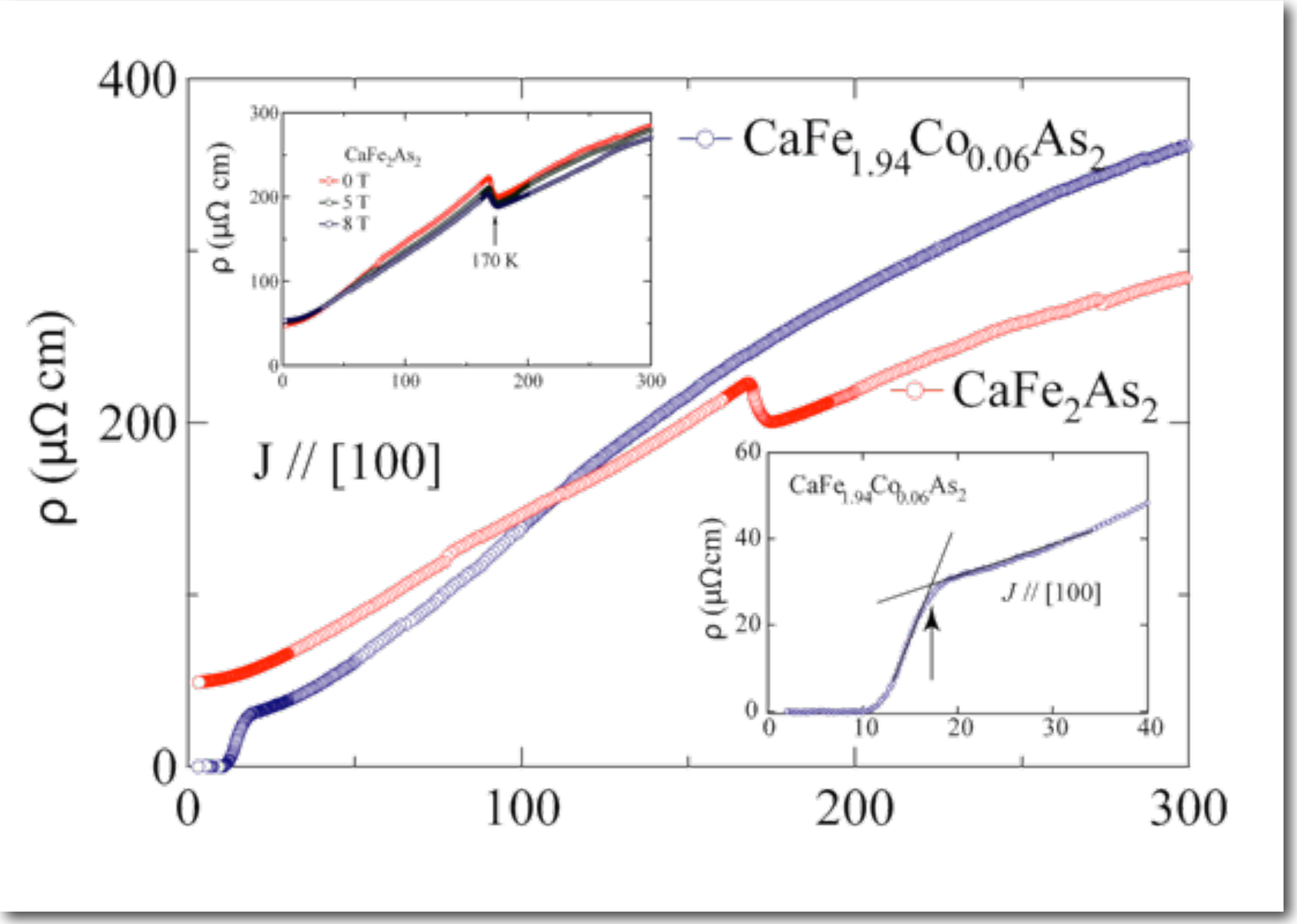


No SDW ordering



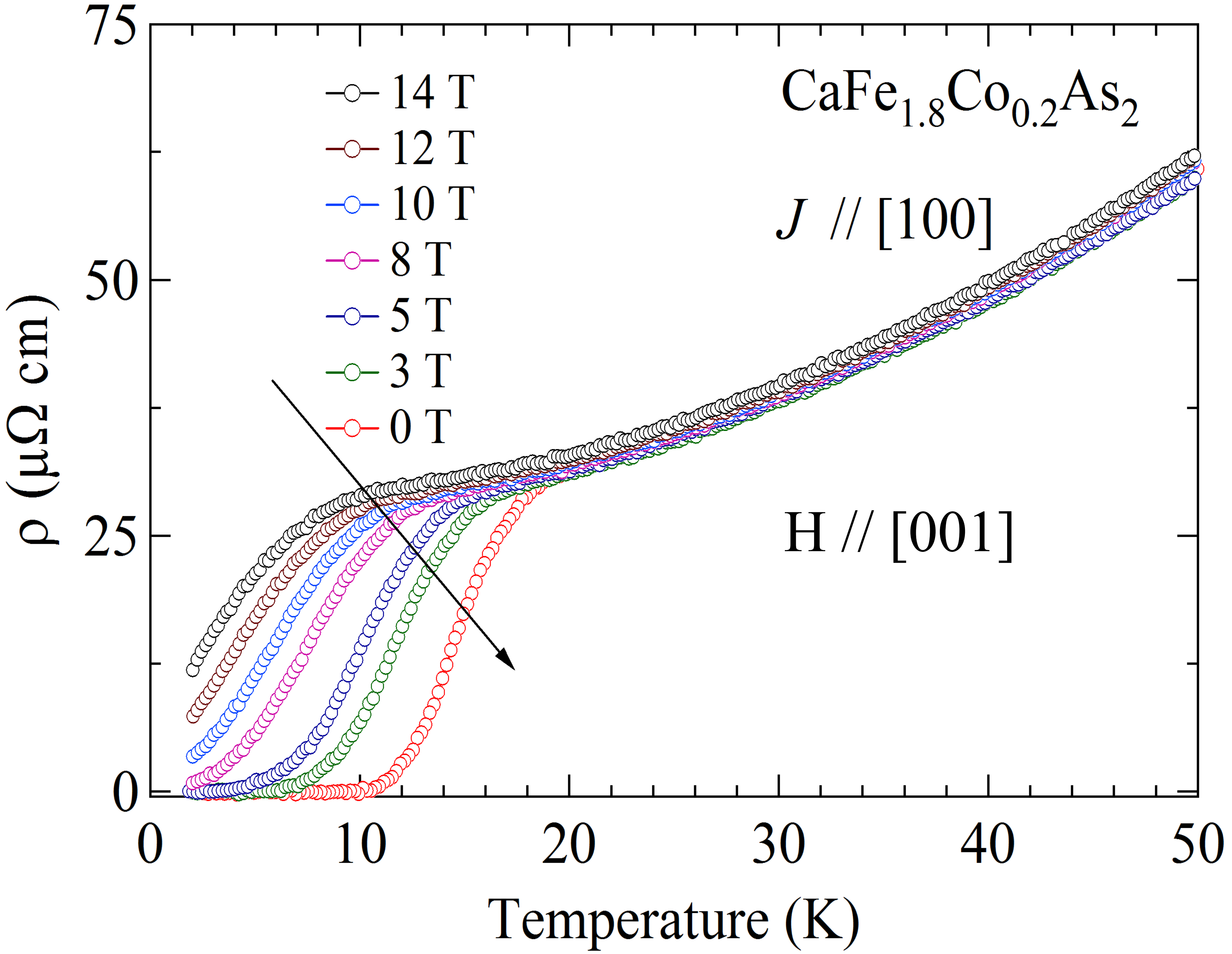
Tc = 17 K

Electrical Resistivity



Increase in resistivity at 170 K is due to the energy gaps introduced into the parts of the Fermi surface by SDW which reduce the number of carriers

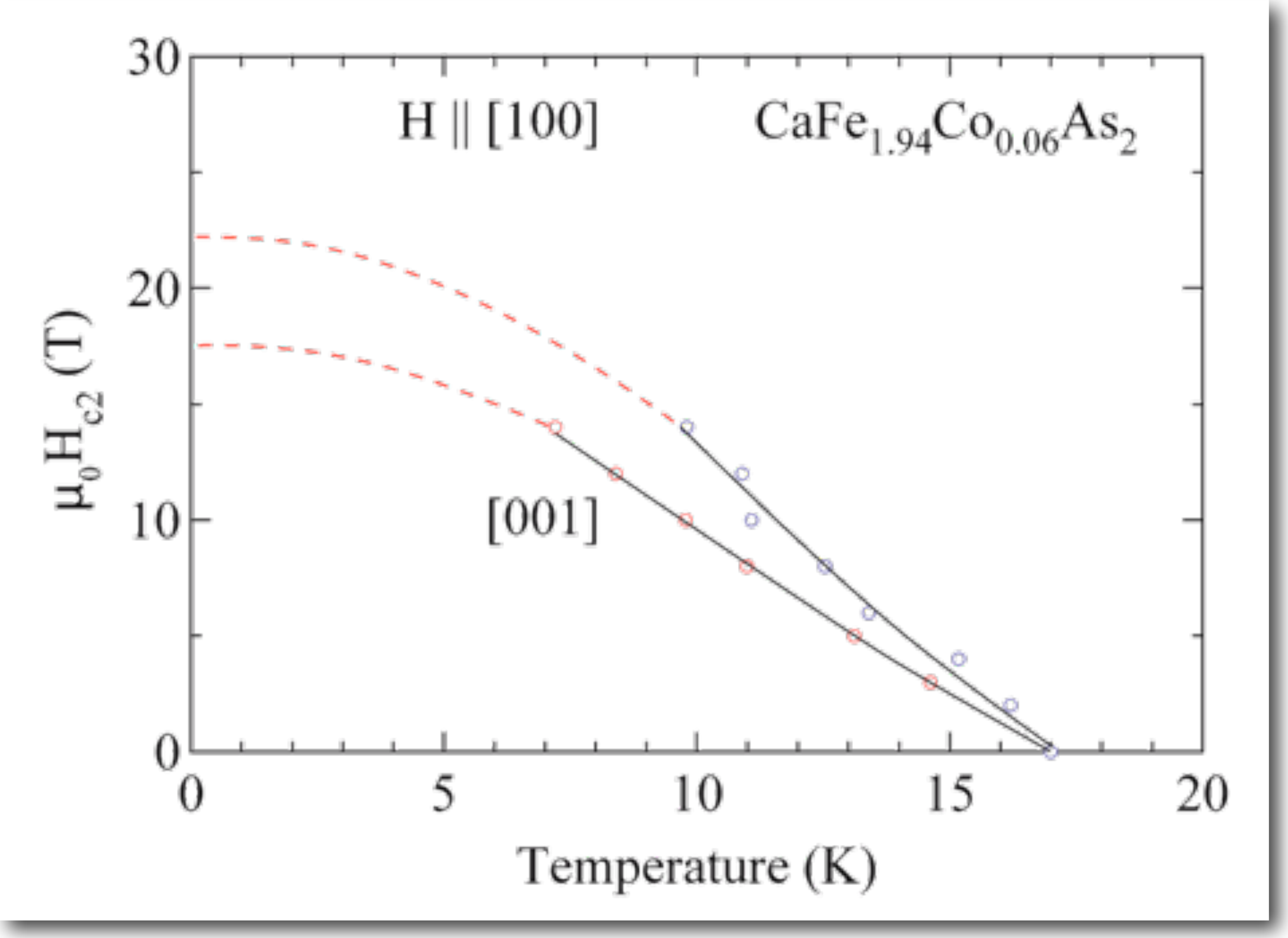
Electrical Resistivity in Applied Magnetic Fields



Neeraj Kumar et al., Phys. Rev. B **79**, 012504 (2009)

Estimation of H_{c2}

Werthamer - Helfand - Hohenberg (WHH) theory



$$H_{c2}(0) = -0.7T_c\left(\frac{dH_{c2}}{dT_c}\right)$$

H // [100]

$$\left(\frac{dH_{c2}}{dT_c}\right) = -1.82\ \mathrm{T/K}$$

H_{c2} = 22 T

H // [001]

$$\left(\frac{dH_{c2}}{dT_c}\right) = -1.43\ \mathrm{T/K}$$

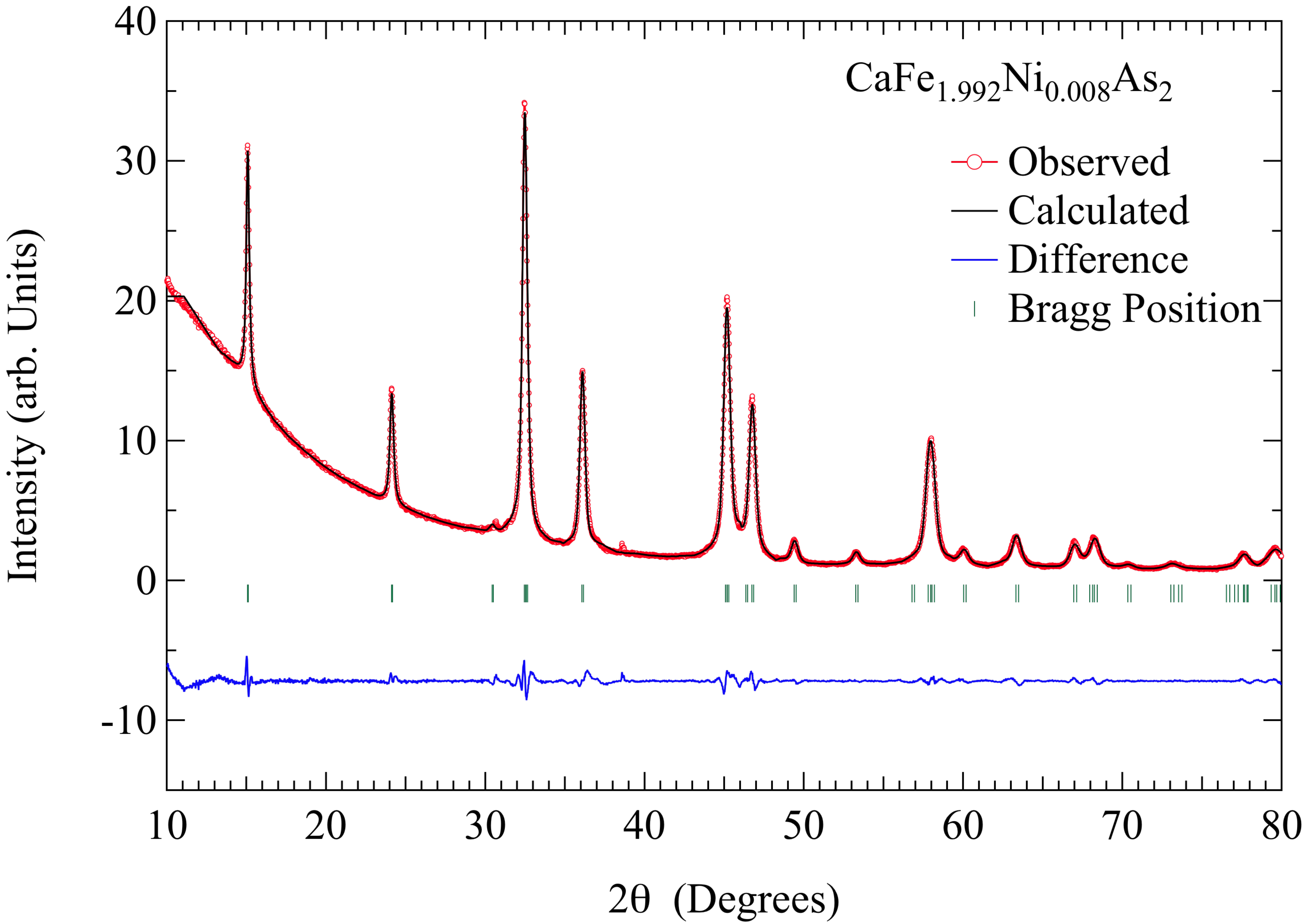
H_{c2} = 17 T

Neeraj Kumar et al., Phys. Rev. B **79**, 012504 (2009)

$CaFe_{2-x}Ni_xAs_2$

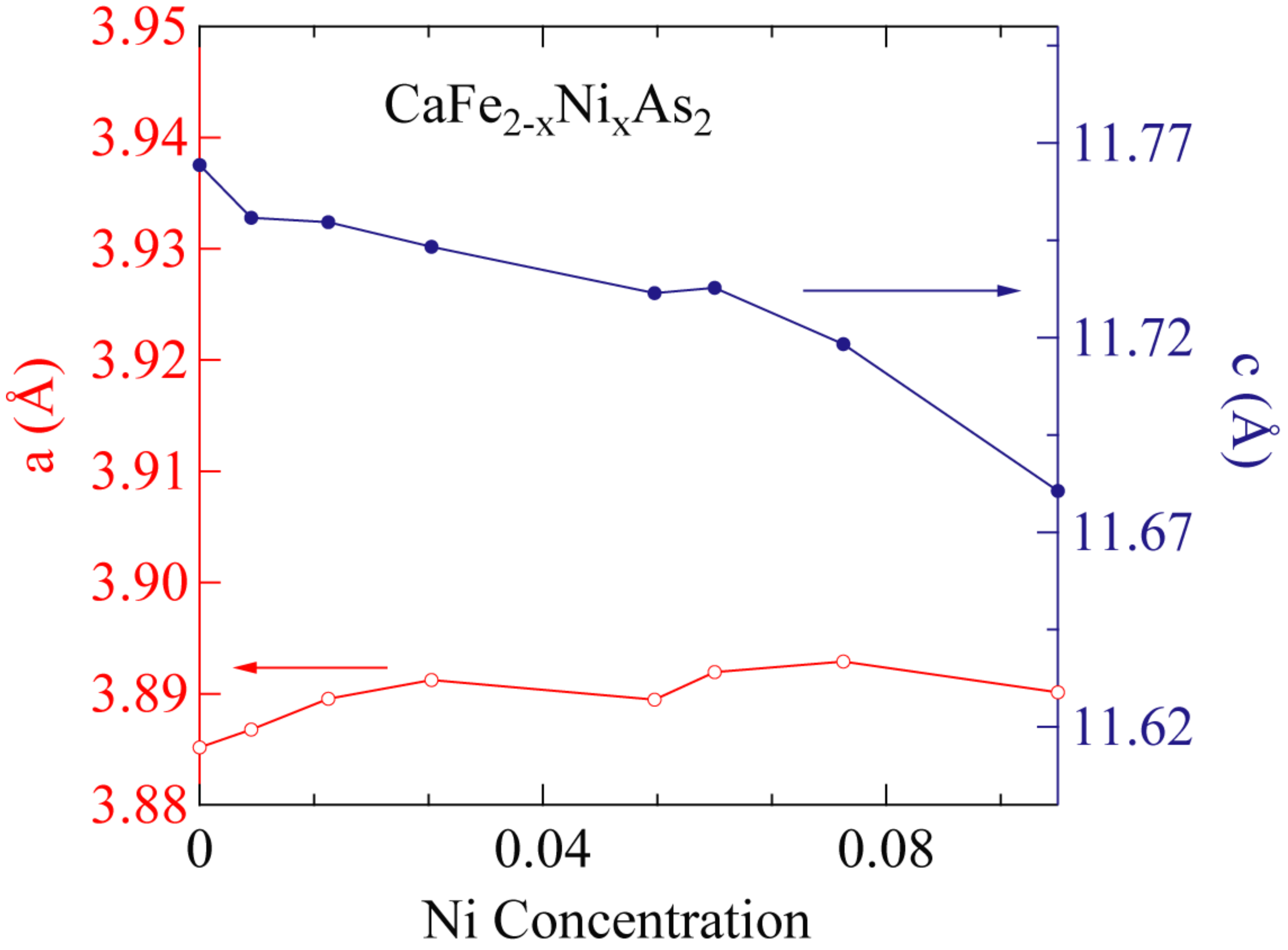
$CaFe_{2-x}Ni_xAs_2$	
Nominal Composition (x)	Actual Composition (x)
0	
0.05	0.006
0.10	0.008
0.15	0.015
0.20	0.020
0.30	0.027
0.40	0.030
0.50	0.053
0.60	0.060
0.80	0.075
1.0	0.1

Rietveld analysis of $CaFe_{2-x}Ni_xAs_2$



Neeraj Kumar et al., Phys. Rev. B **80** (2009) 144524

Variation of lattice constant with Ni doping

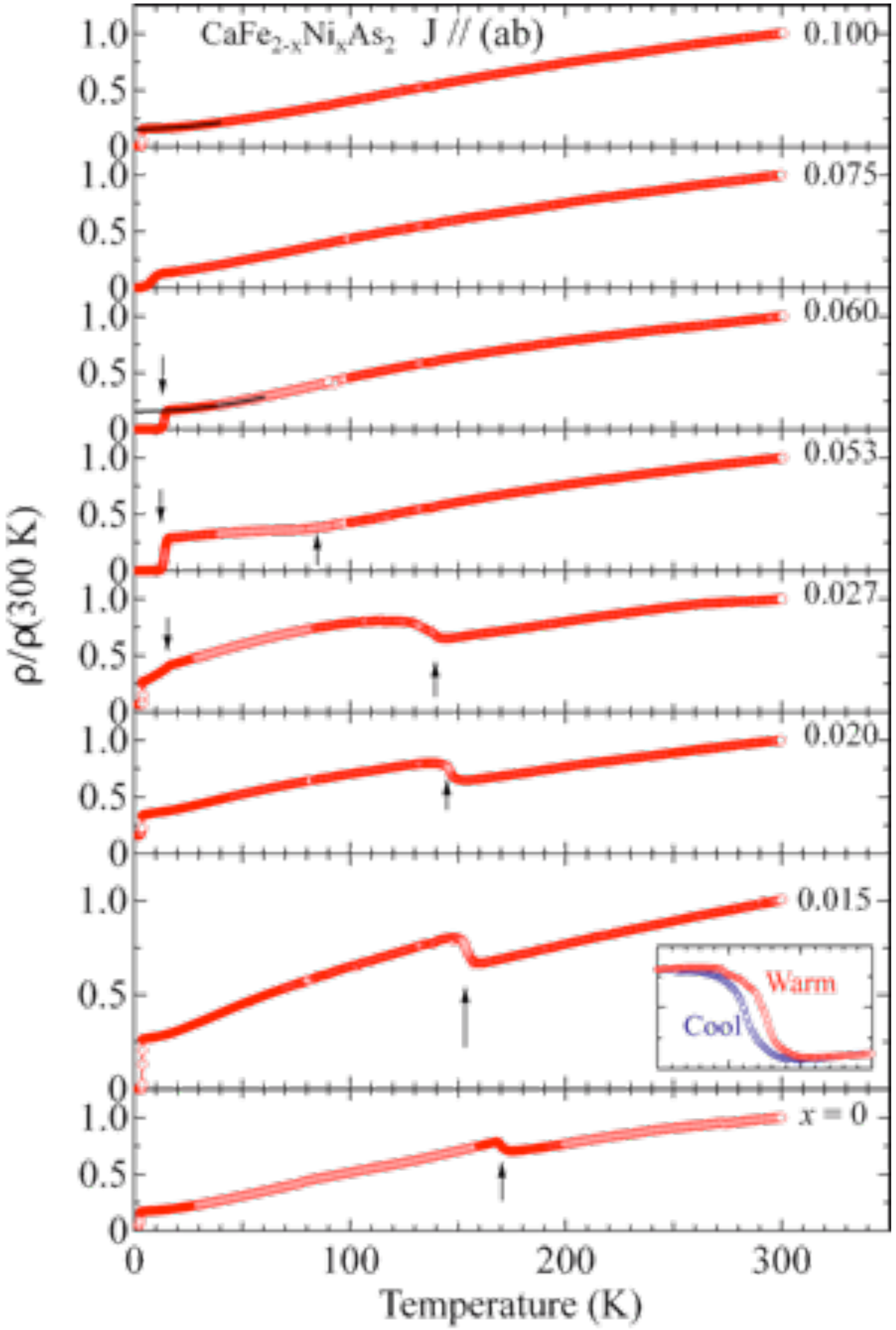


Unit cell volume decreases

Neeraj Kumar et al., Phys. Rev. B **80** (2009) 144524

Electrical Resistivity of $CaFe_{2-x}Ni_xAs_2$

Tc = 15 K for x = 0.06



No superconductivity

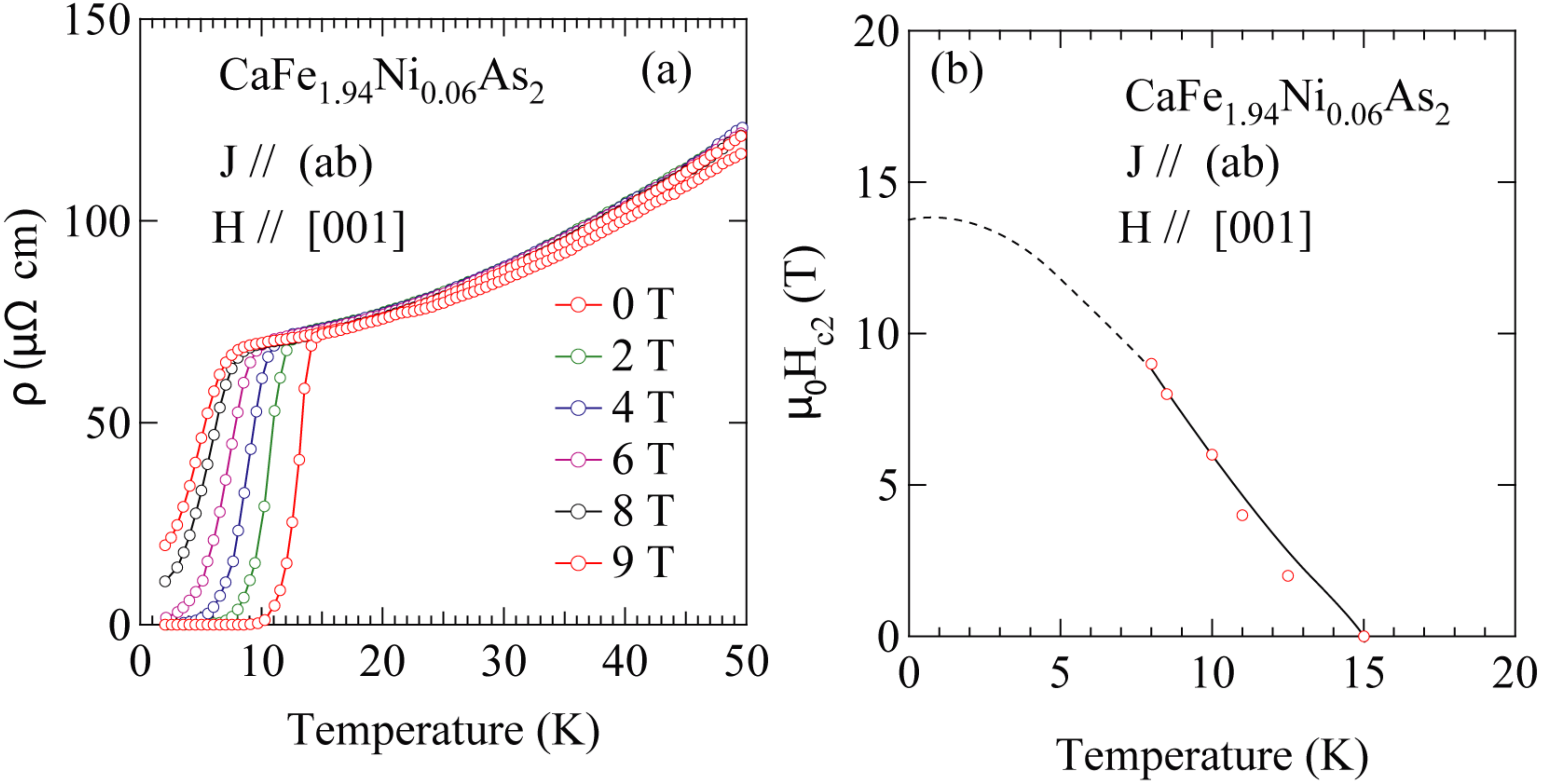
Superconductivity

Co-existence of magnetism & superconductivity

T_{SDW} decreases with Ni doping

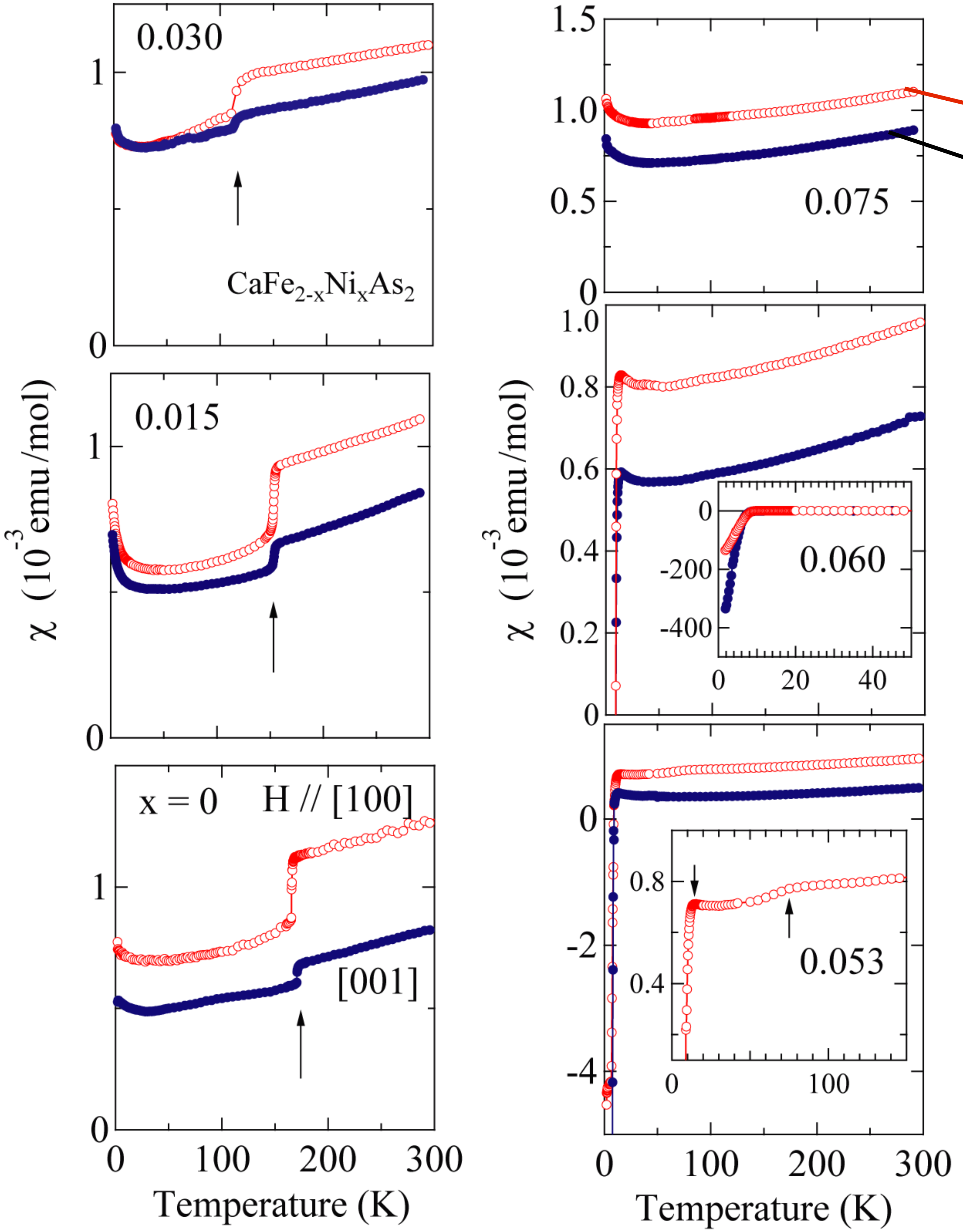
Neeraj Kumar et al., Phys. Rev. B **80** (2009) 144524

Hc2 of $CaFe_{1.94}Ni_{0.06}As_2$



H_{c2} = 14 T for H // [001]

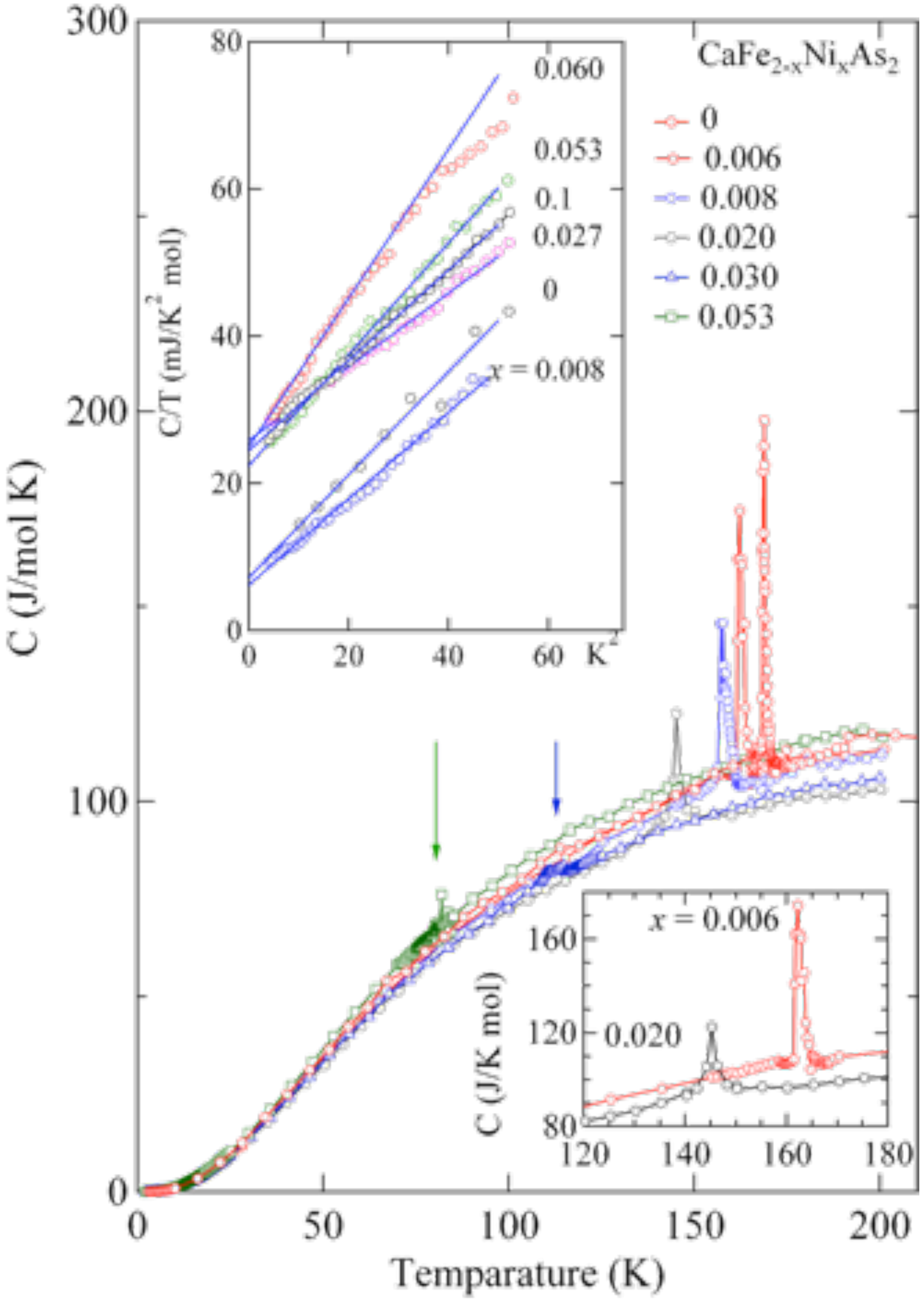
Magnetic susceptibility of $CaFe_{2-x}Ni_xAs_2$



H // [100]

H // [001]

Heat capacity of $CaFe_{2-x}Ni_xAs_2$



γ increases for x ≥ 0.027

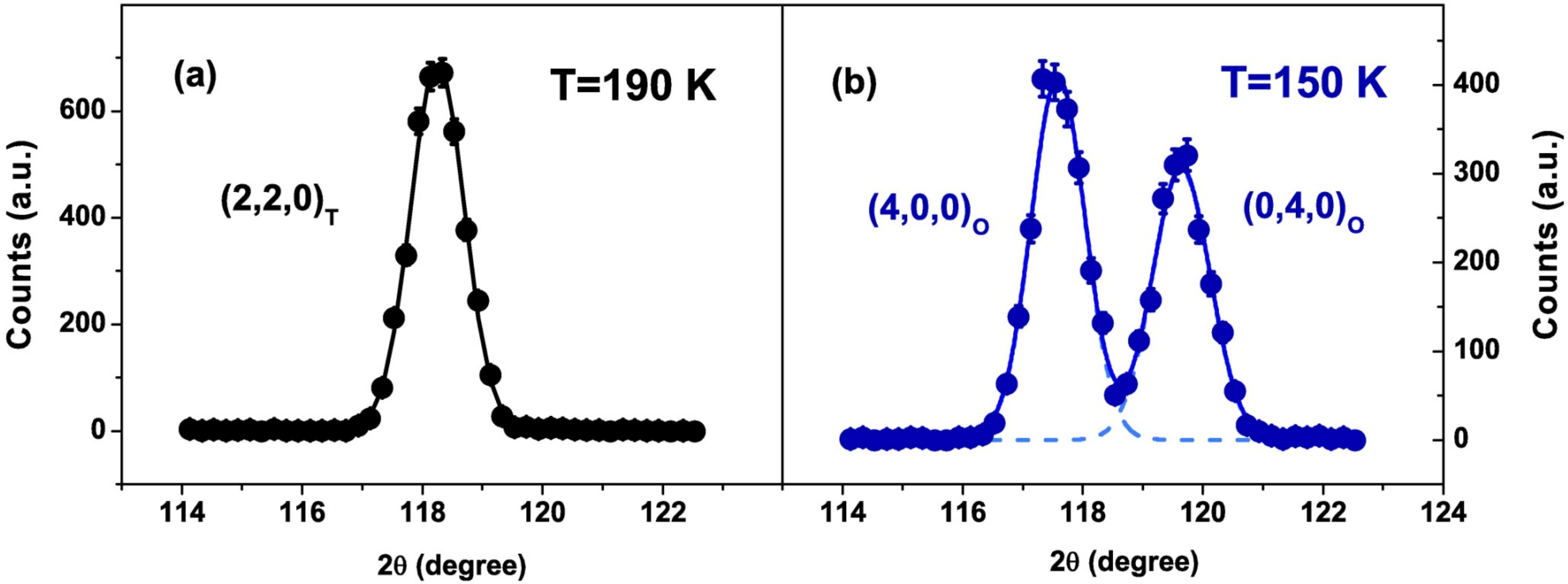
suggests appreciable enhancement of density of states at the Fermi level

Single crystal neutron diffraction

BT-7 and BT-9 triple axis spectrometer at NIST center for Neutron Research

Neutron wavelength: 2.359 Å

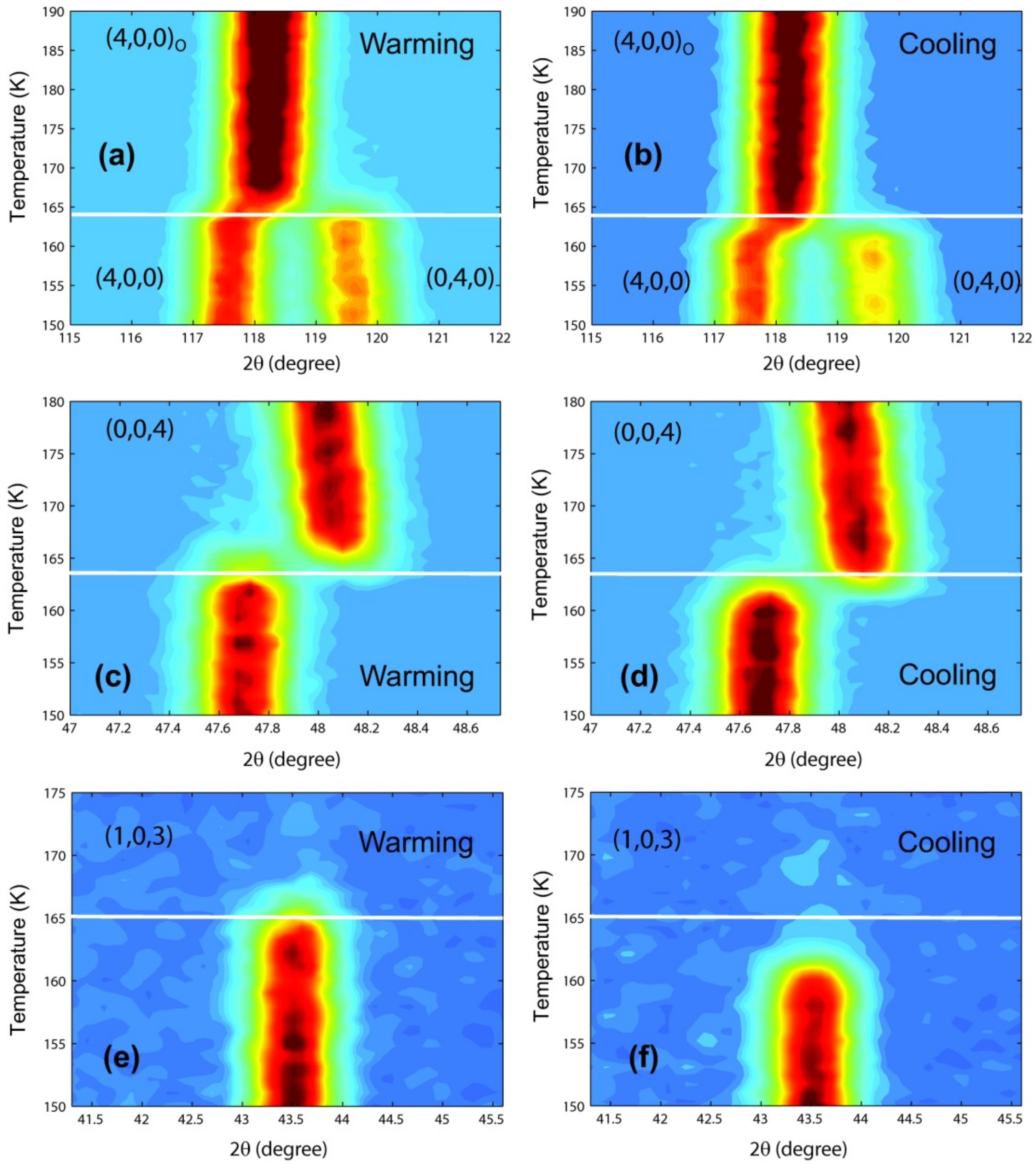
Pyrolyic graphite (PG) monochromator



Tetragonal (220) reflection spits into orthorhombic (400) and (040)

Neeraj Kumar et al., Phys. Rev. B **80** (2009) 144524

Intensity maps of structural & magnetic Bragg peaks in $CaFe_{1.994}Ni_{0.006}As_2$



Below T_{SDW} peaks are not symmetric about the tetragonal position - Change in the area of the *ab*-plane - decrease in the area of orthorhombic phase

Below T_{SDW} sudden decrease in the position of the *c*-axis lattice parameter. This tends to compensate for the decrease in the area of the *ab*-plane

Sudden appearance and disappearance of the magnetic peak on warming and cooling

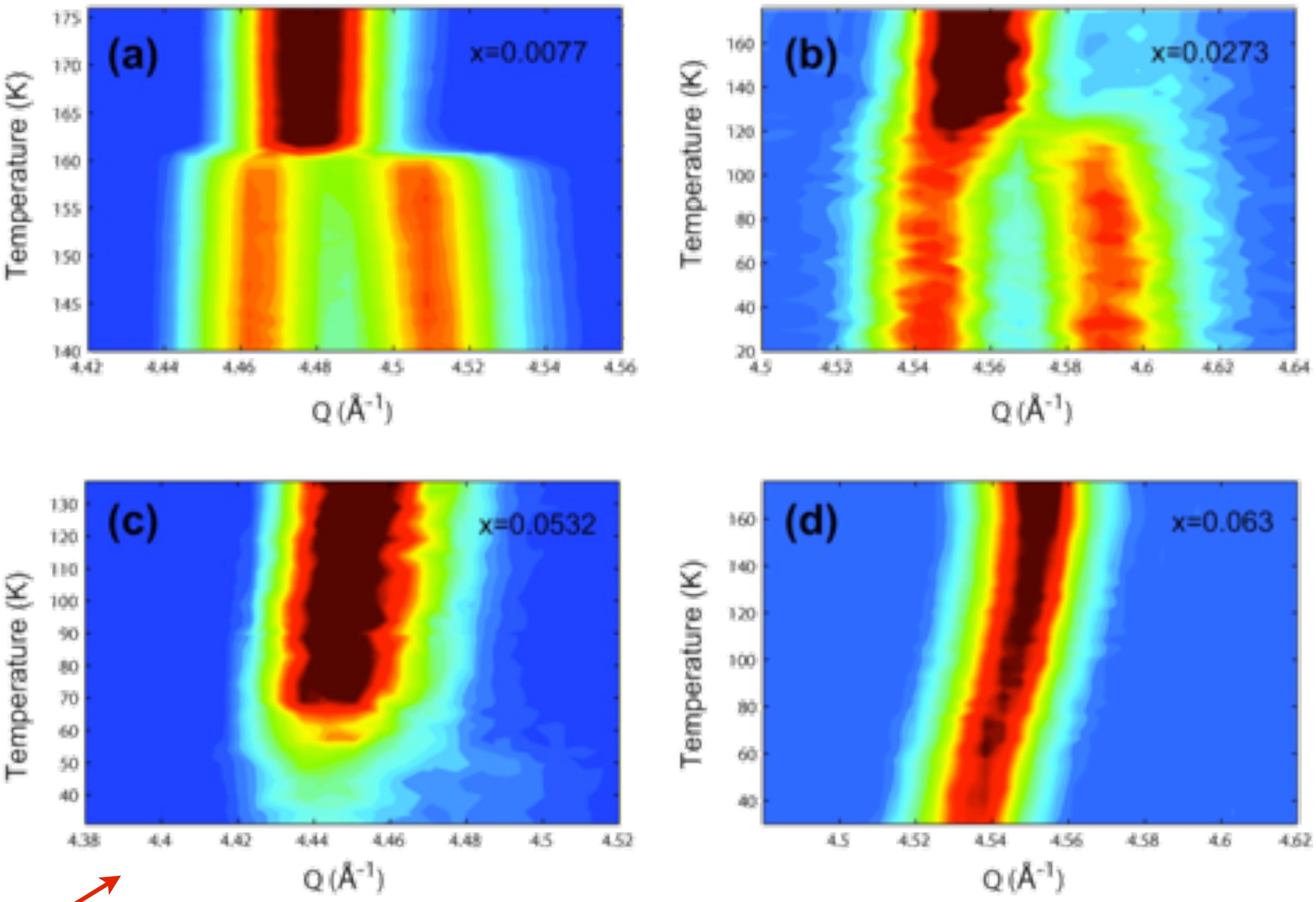
Neeraj Kumar et al., Phys. Rev. B **80** (2009) 144524

Nature of orthorhombic distortion as a function of doping

Temperature maps of $(2,2,0)_T$ to $(4,0,0)_O$, $(0,4,0)_O$ peaks for 4 different compositions:

x = 0.007

x = 0.027



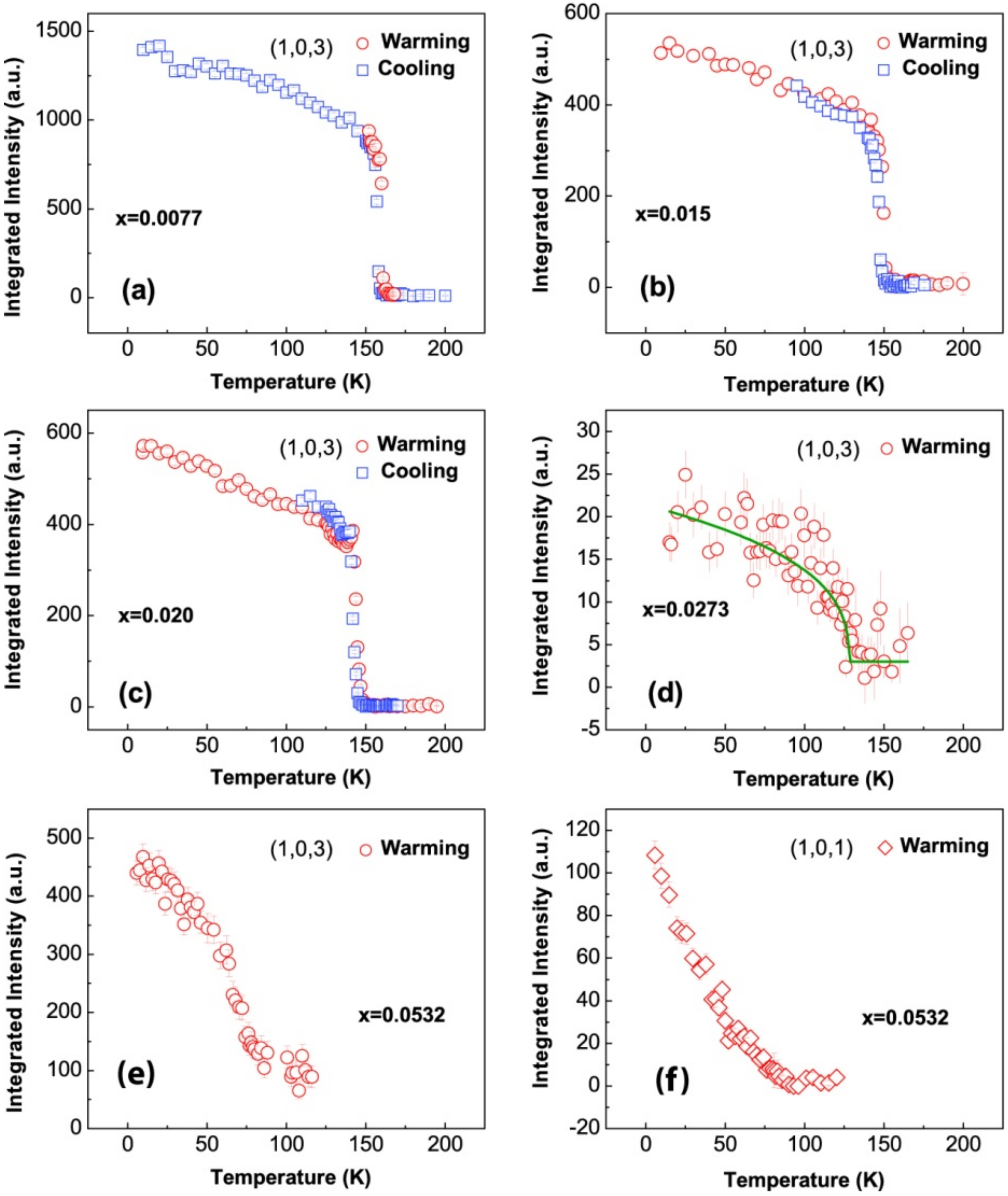
x = 0.05

x = 0.06

When Tc sets in the distortion very weak

For x = 0.06, where superconductivity occurs, there is no structural distortion.

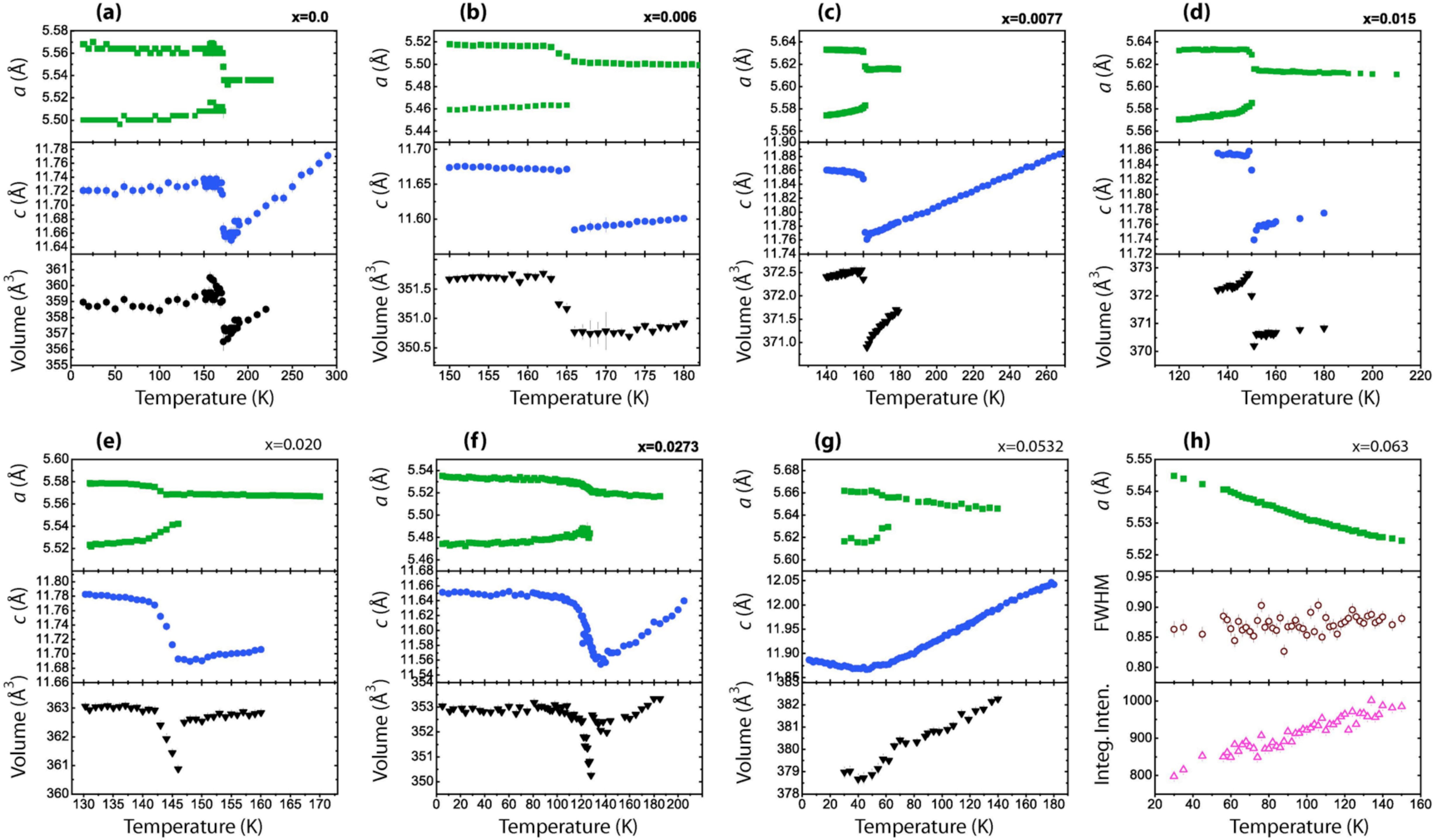
Temperature dependence of (103) magnetic Bragg peak for various concentration of Ni doping



for small *x* there is a jump in the magnetic scattering intensity - First order

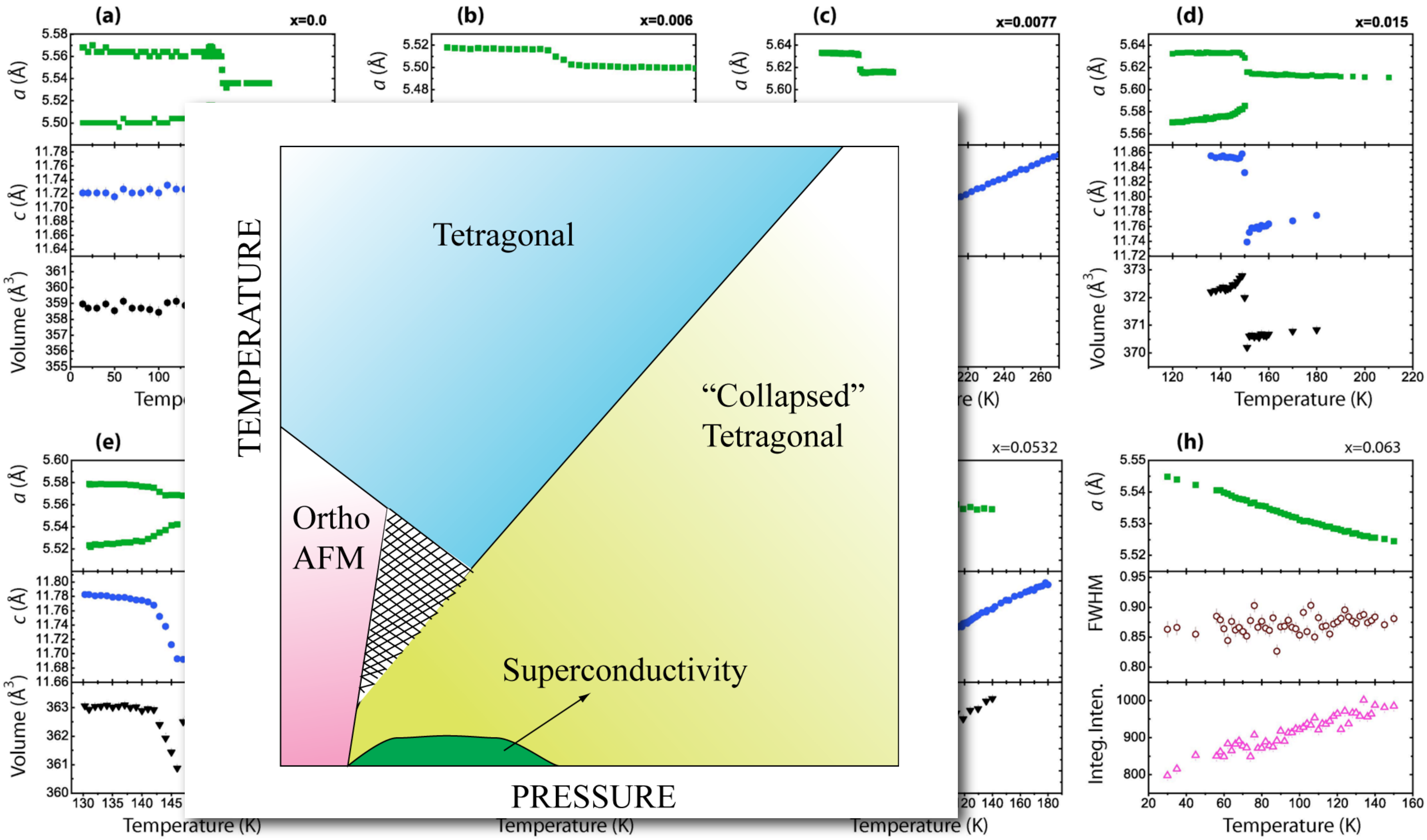
At higher *x* the ordered moment is smaller and the transition appears to be continuous

Temperature dependence of the lattice constants for various Ni concentration



In the superconducting state the structural transition does not occur

Temperature dependence of the lattice constants for various Ni concentration

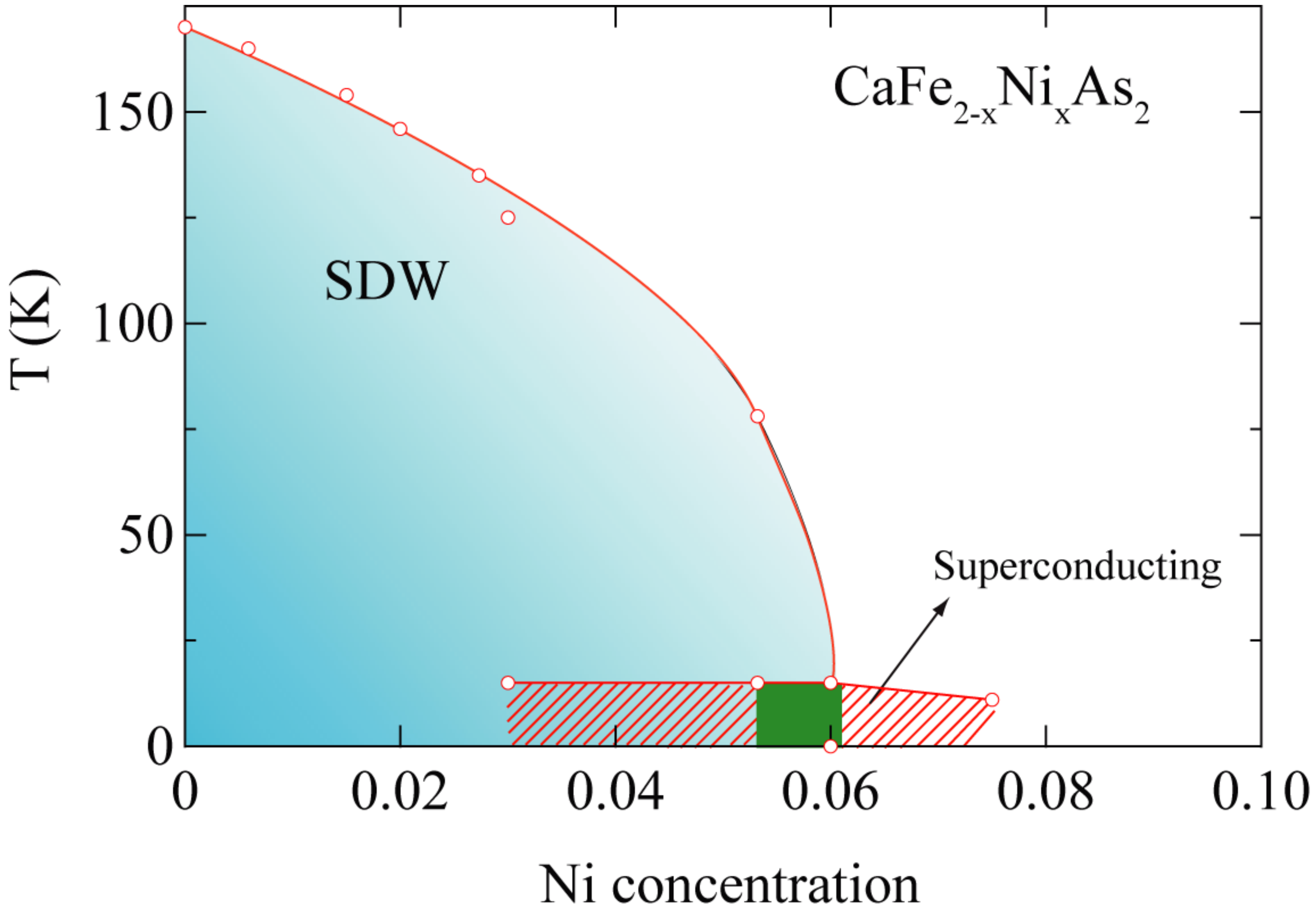


In the superconducting state the structural transition does not occur

From Neutron diffraction:

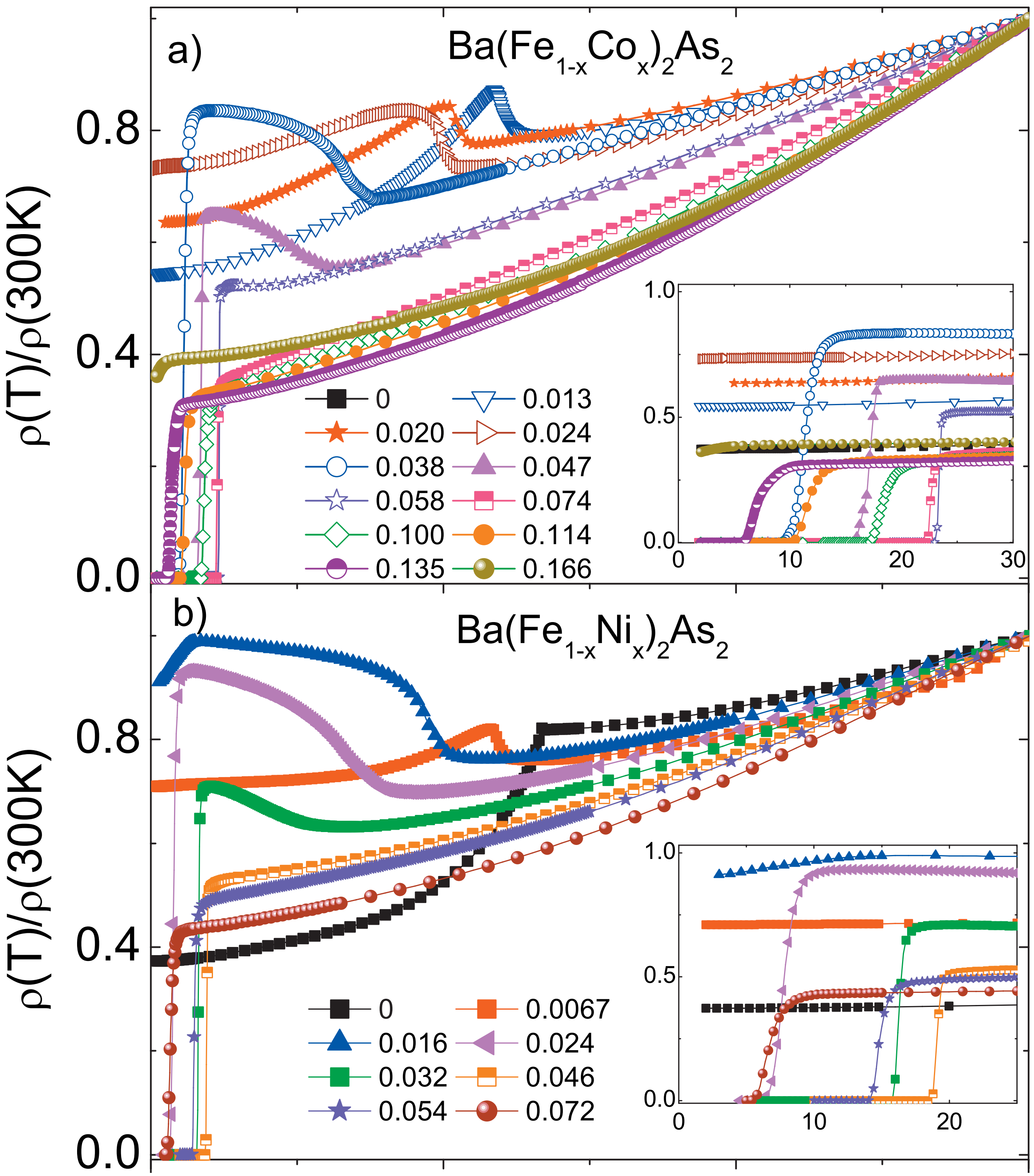
Ni Doping	Structural Transition (K)	Magnetic ordering	Ordered moment (μ_B)
0	172	172	0.8
0.008	161	160.9	0.728
0.015	151	150.9	0.621
0.020	146	148	0.162
0.0273	129	128.3	0.058
0.0532	80	80	0.037
0.063	No transition	No transition	No moment

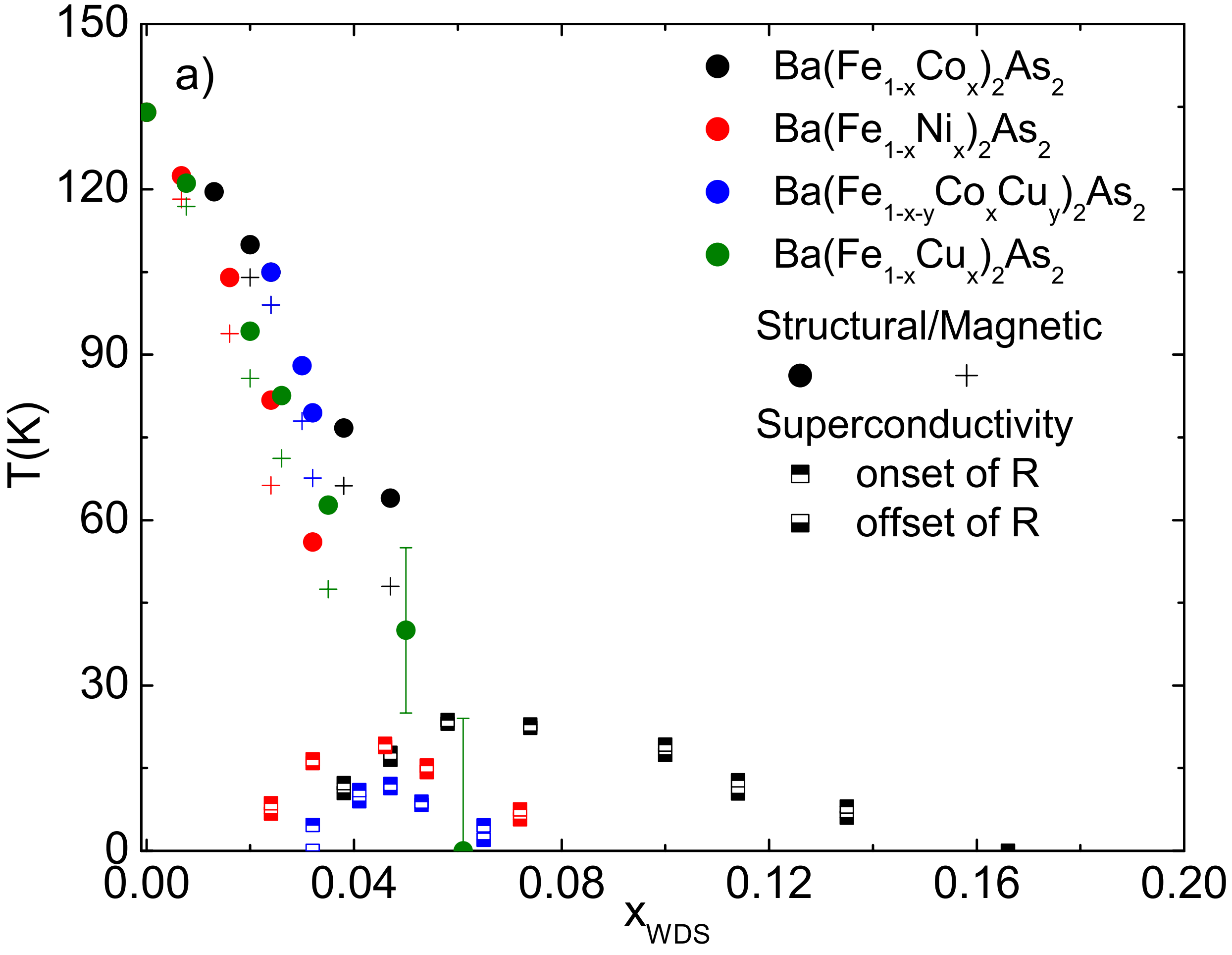
Phase diagram of $CaFe_{2-x}Ni_xAs_2$



Neeraj Kumar et al., Phys. Rev. B **80** (2009) 144524

TM doping in $BaFe_{2-x}T_xAs_2$ (T = Co and Ni)



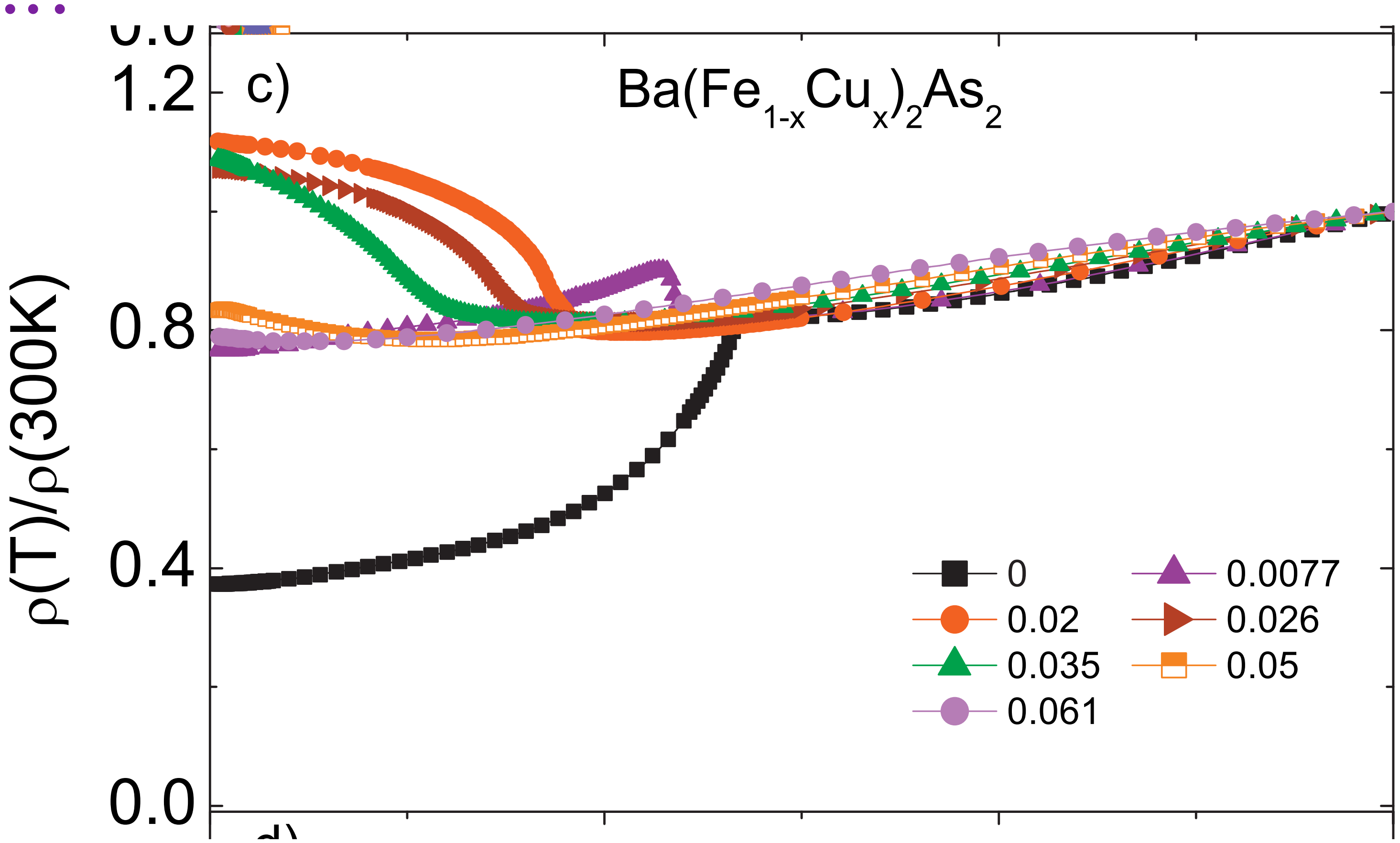


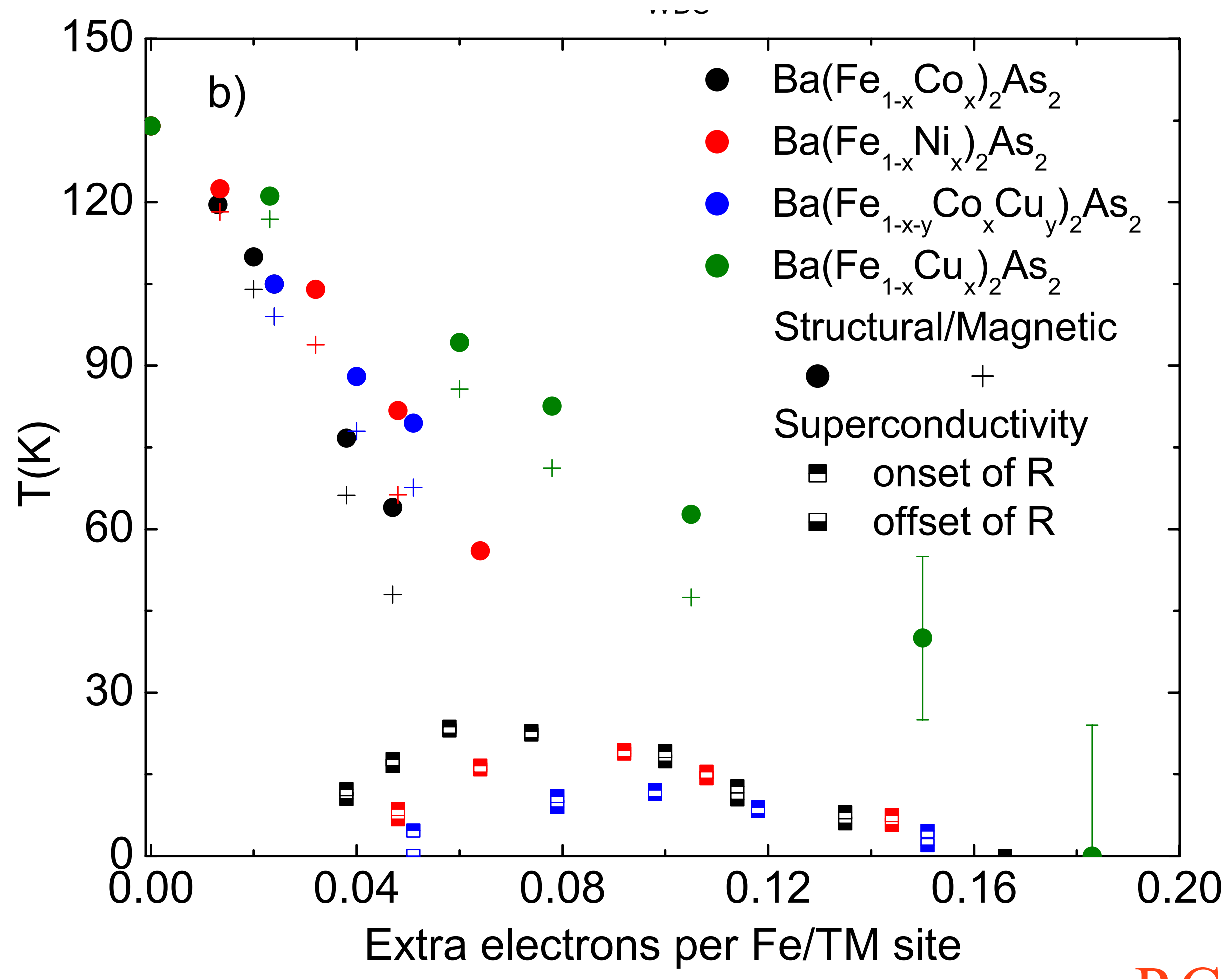
P.C. Canfield et al., Phys. Rev. B **80** (2009) 060501(R)

Suppression of the structural/antiferromagnetic transition is a **necessary** condition for observing superconductivity in these compounds

But...!!

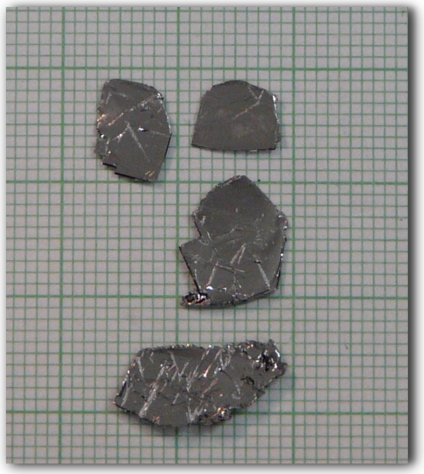
It is not a sufficient condition...!





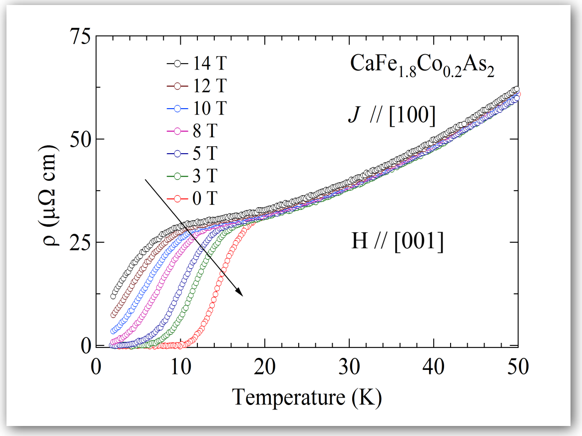
P.C. Canfield et al., Phys. Rev. B **80** (2009) 060501(R)

Summary



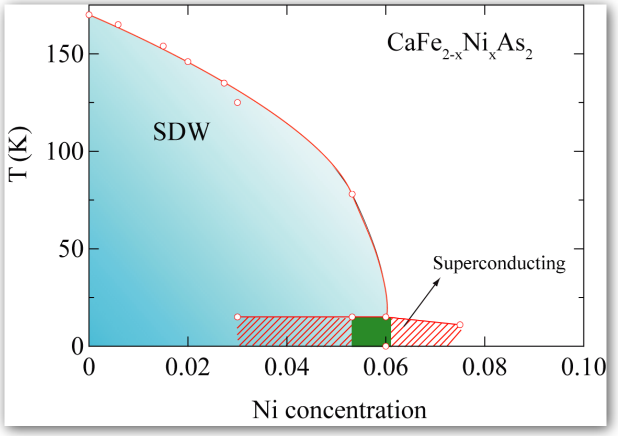
Successfully grown the single crystals of AFe_2As_2

Superconductivity is observed by electron doping in the tetragonal phase of $CaFe_{2-x}T_xAs_2$



Superconductivity is observed for an optimum doping concentration of $x = 0.06$

A phase diagram has been constructed based on the systematic study of Ni-doping in $CaFe_{2-x}Ni_xAs_2$



Thank you....!!!

Group Website: http://www.tifr.res.in/~crystalgrowth

Personal Website: http://www.thamizhavel.com