Nadprzewodniki na bazie żelaza w świetle badań spektroskopią mössbauerowską

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02-03-2018
Seminarium Wydziału Fizyki i Informatyki Stosowanej
AGH

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  - AFe_2As_2 (A = Ca, Ba, Eu)
  - $Ba_{1-x}K_xFe_2As_2$ and $SmFeAsO_{1-x}F_x$
  - $BaFe_2(As_{1-x}P_x)_2$
- Conclusions

Superconductivity in the non-magnetic state of iron under pressure

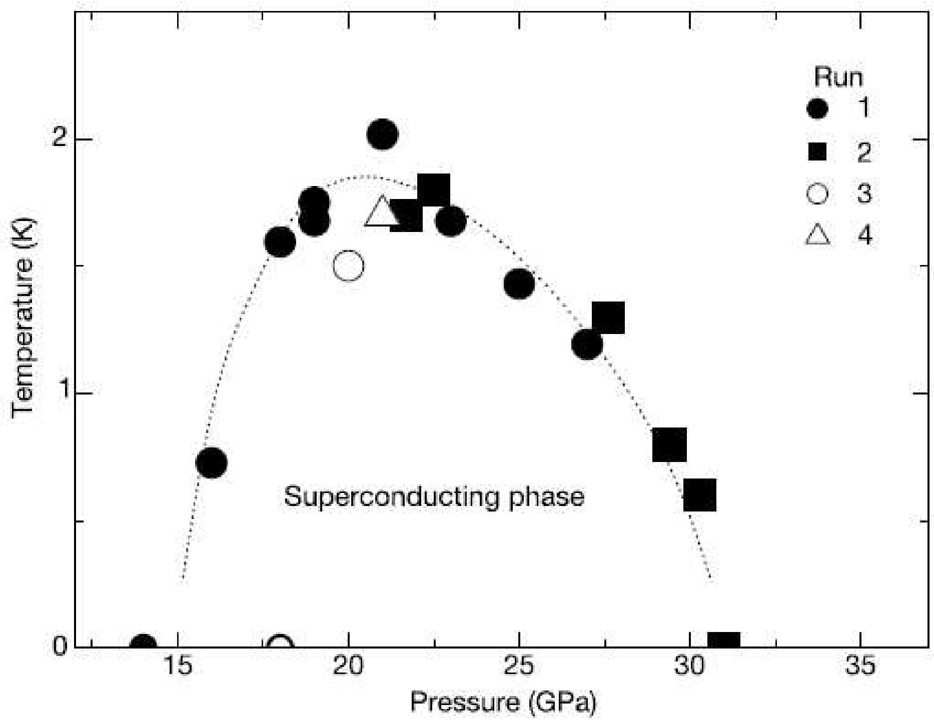
K. Shimizu *et al*. Nature **412**, 316 (2001)

hcp Fe

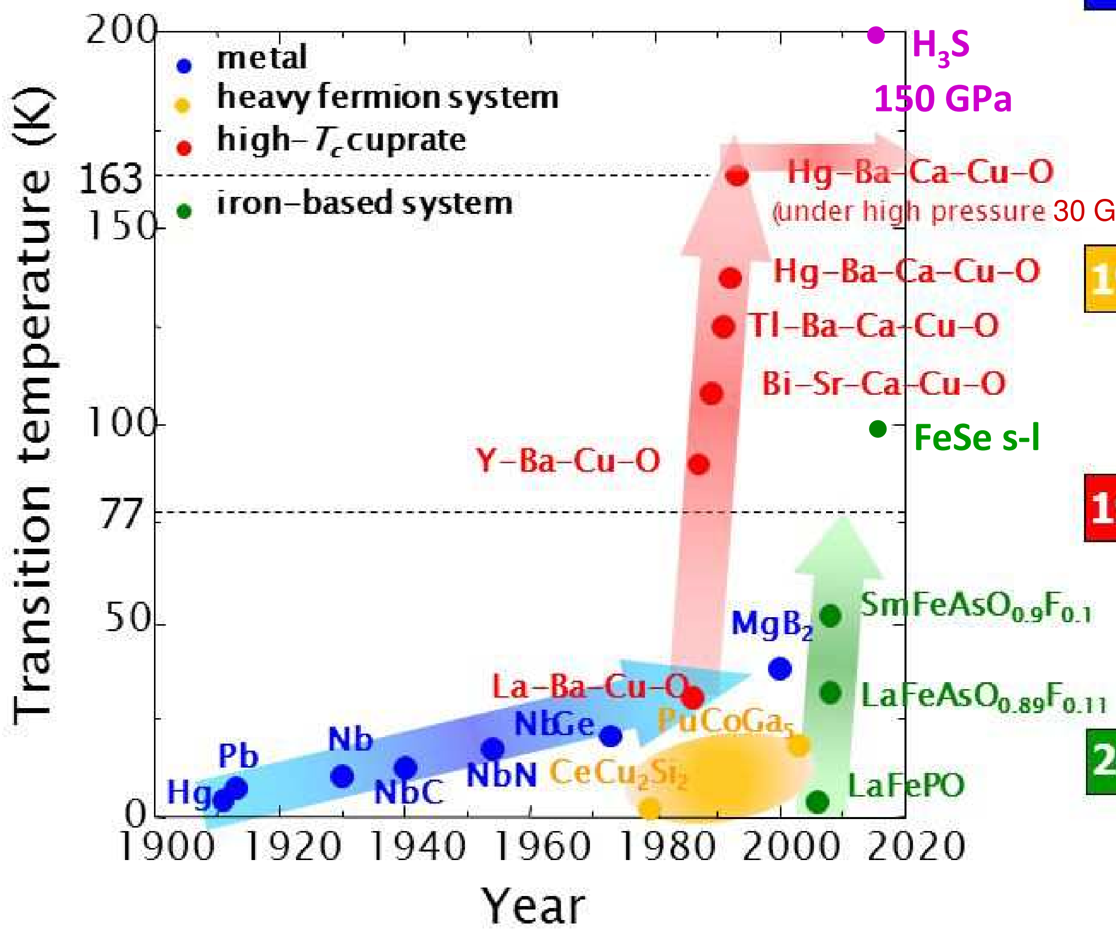
becomes superconductor

at temperatures below **2 K**

and at pressures between **15** and **30 GPa**



History of Superconductivity



1911
Discovery of superconducting phenomenon

1979
Heavy fermion superconductor

1986
High-T_c cuprate superconductor

2006
Iron-based high-T_c superconductor

Up to now the maximum T_{sc} is **56 K**

J|A|C|S COMMUNICATIONS

Published on Web 02/23/2008

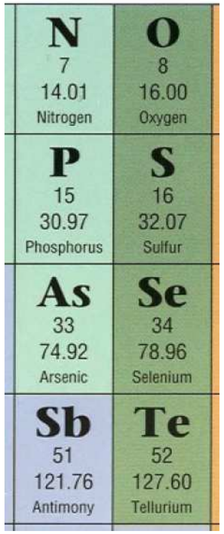
Iron-Based Layered Superconductor La[$O_{1-x}F_x$]FeAs (x = 0.05−0.12) with T_c = 26 K

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

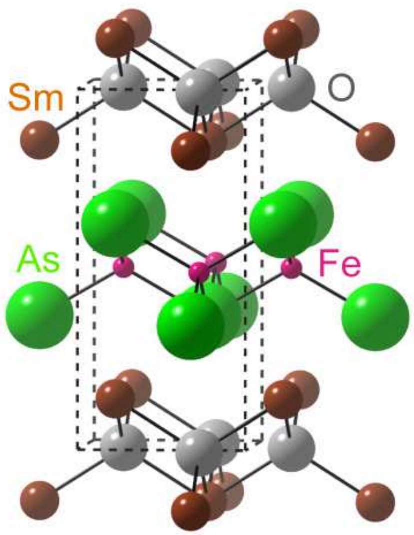
Fe-based Superconducting Families

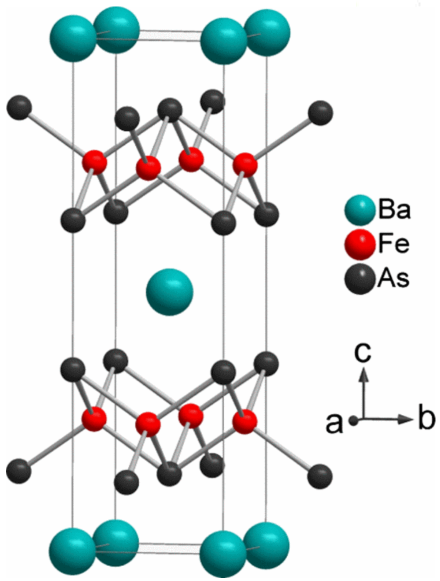
pnictogens: P, As

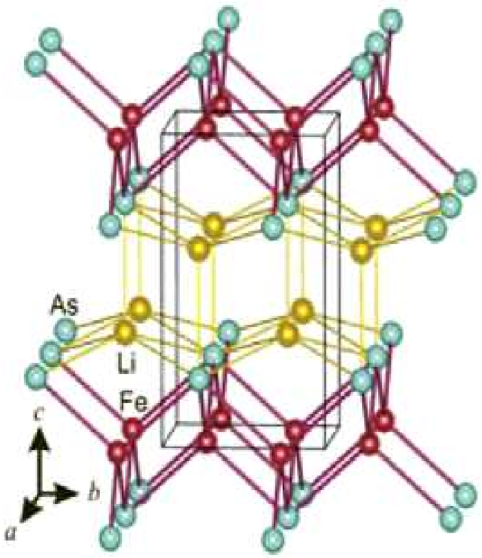
chalcogens: S, Se, Te

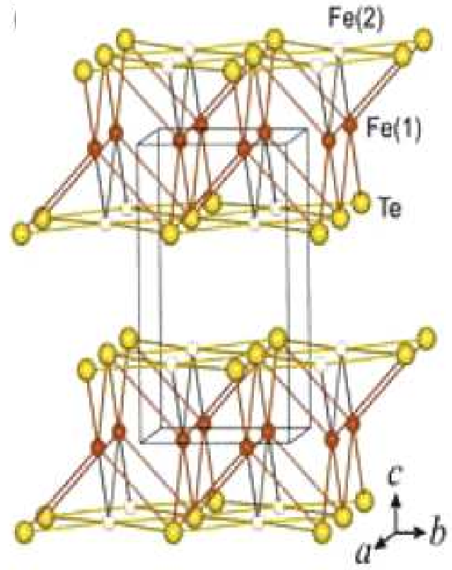


1111	122	111	11
LnO(F)FeAs	AFe_2As_2	AFeAs	FeTe(Se,S)
Ln = La, Ce, Pr, Nd, Sm, Gd …	A = Ca, Sr, Ba, Eu, K	A = Li , Na	



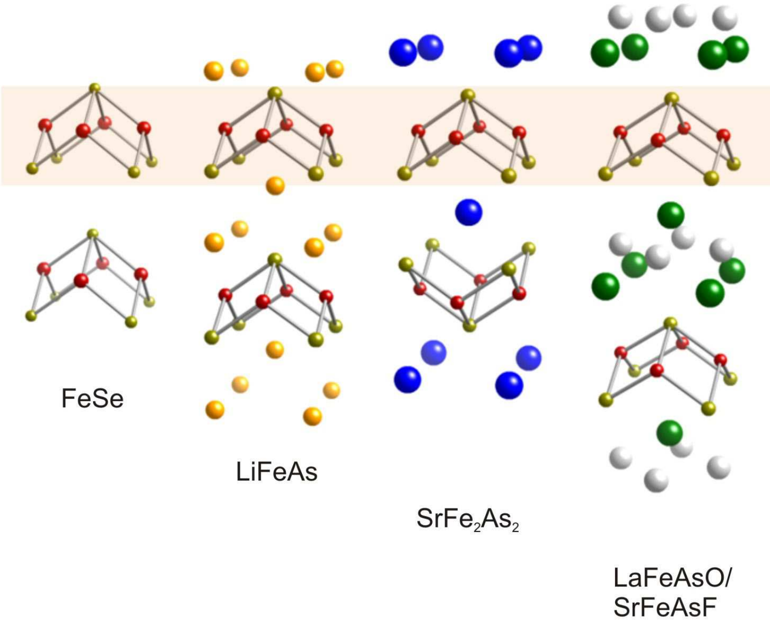


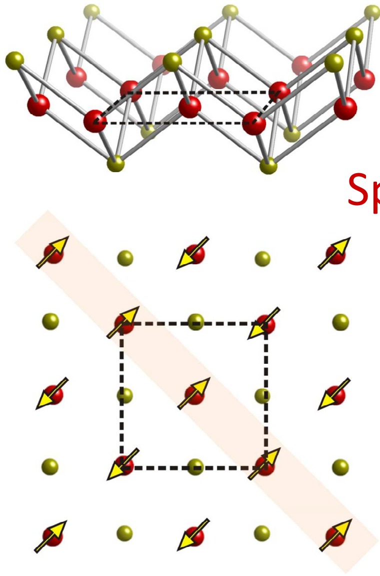




T_{sc} *max* = 56 K	47 K	18 K	15 K

Layered Structure of Fe-based Superconductors

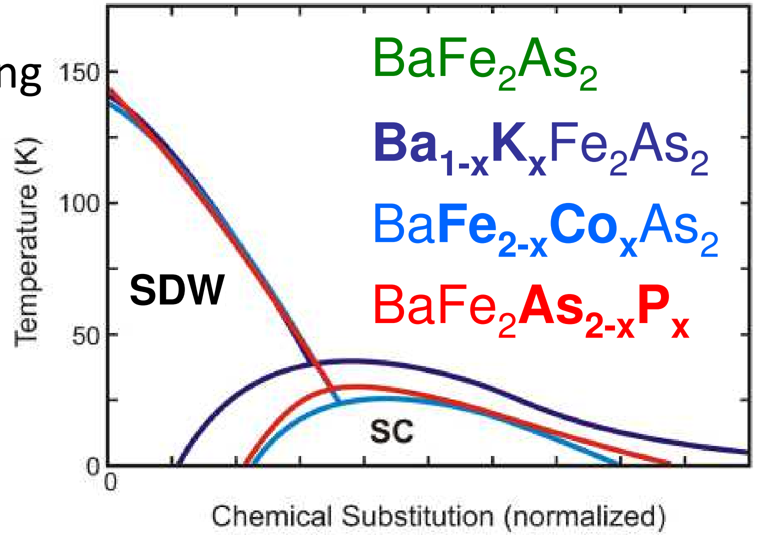




Spin density wave (SDW) magnetic order

Phase Diagram

Holes, electrons or isovalent doping



Parent Compounds

Compound	$T_{N\ Fe/R}$ (K)	$\mu_{Fe\ /\ R}$ (μ_B)
LaFeAsO	137	0.4 – 0.7
CeFeAsO	140	0.8
NdFeAsO	141 / 2	0.5
GdFeAsO	133 / 4	
$CaFe_2As_2$	170	0.8
$BaFe_2As_2$	140	0.9
$EuFe_2As_2$	190 / 19	1.0 / 5.9
$Fe_{1.1}Te$	70	2.2

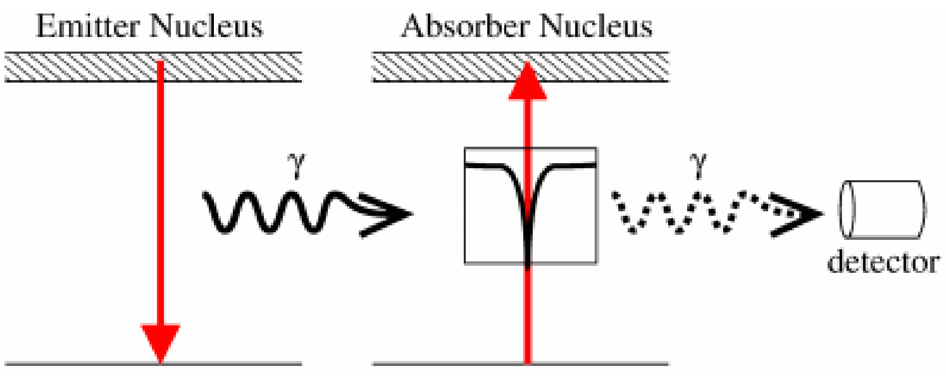
Doped Compounds

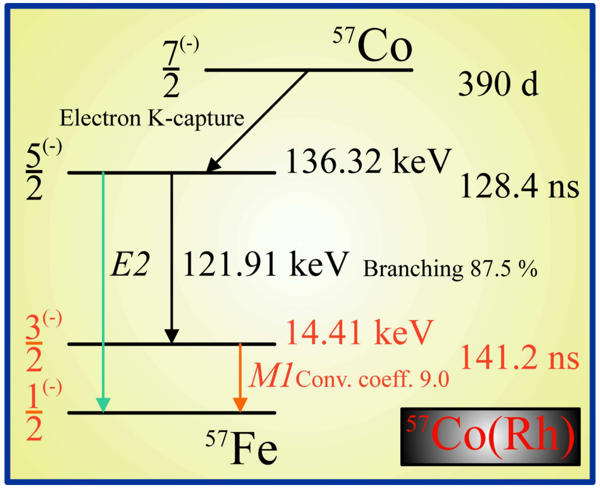
⇓

Superconductors

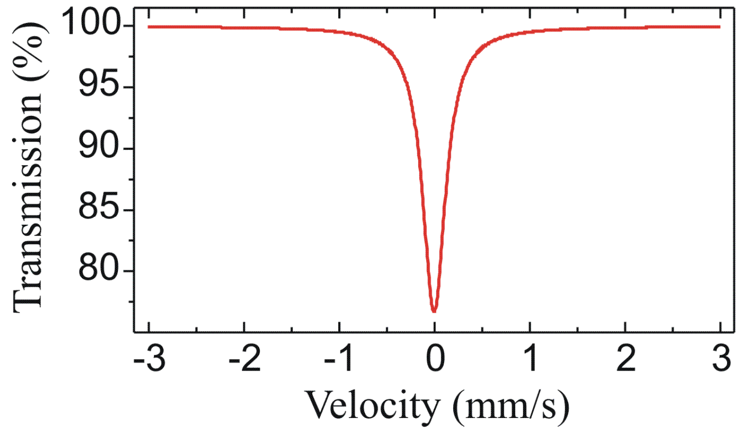
Compound	T_c (K)
$LaFeAsO_{0.89}F_{0.11}$	26
$NdFeAsO_{1-y}$	54
$SmFeAsO_{1-x}F_x$	55
$Gd_{0.8}Th_{0.2}FeAsO$	56
$LaFePO_{1-x}F_x$	5
$Ba_{0.6}K_{0.4}Fe_2As_2$	38
$BaFe_{1.8}Co_{0.2}As_2$	23
$BaFe_2As_{1.3}P_{0.7}$	30
$Eu_{0.5}K_{0.5}Fe_2As_2$	32
KFe_2As_2	4
LiFeAs	18
LiFeP	6
FeSe	8
$FeTe_{0.6}Se_{0.4}$	15

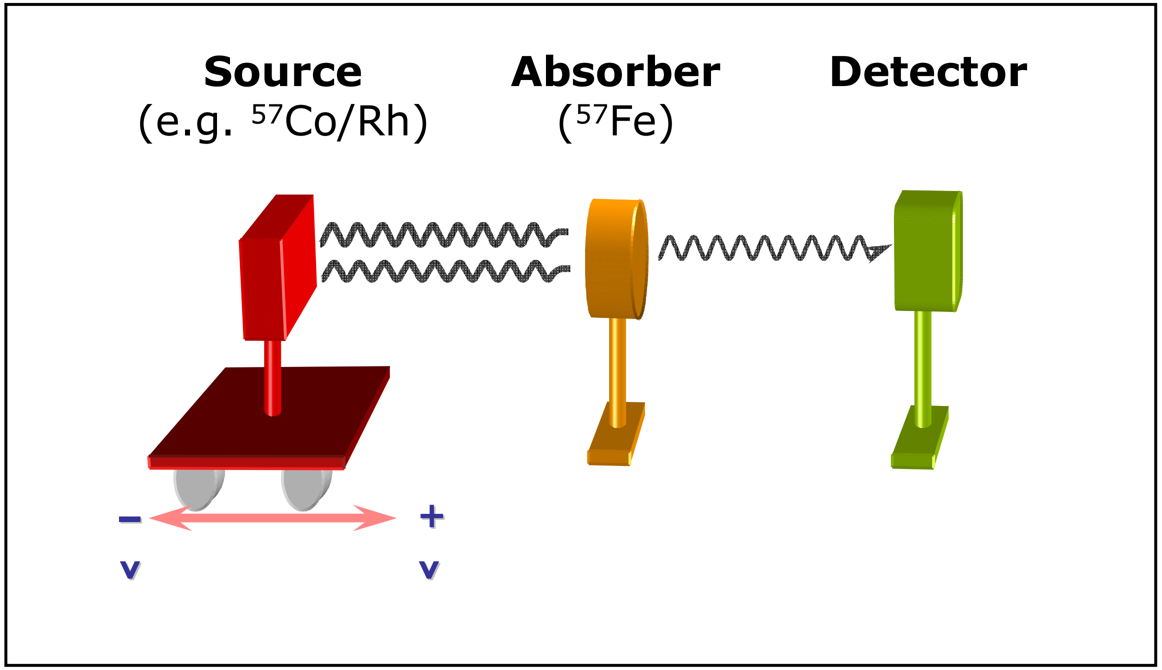
Mössbauer Spectroscopy





γ-ray energy is modulated by the Doppler effect due to the source motion vs. absorber





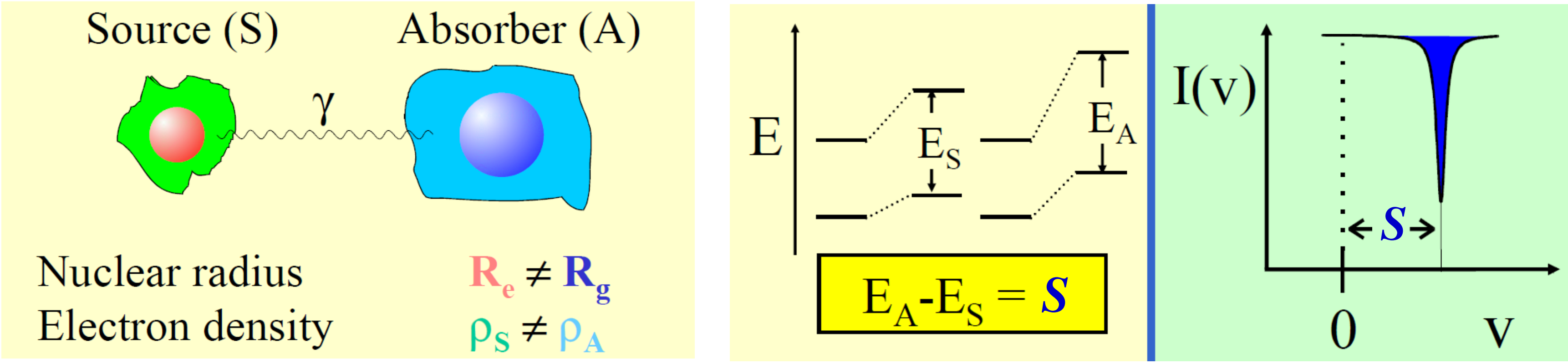
1 mm/s → 48 neV

$$\Gamma_0 = 0.096 \text{ mm/s}$$

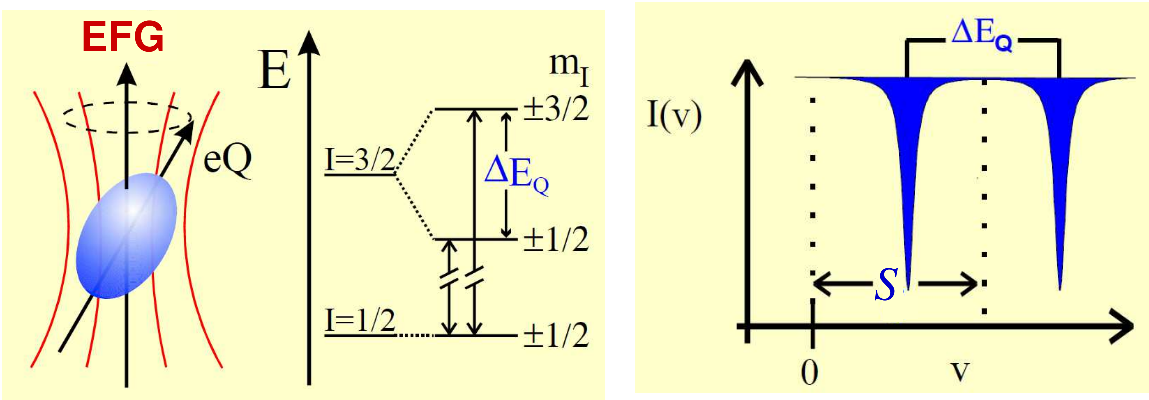
$$\frac{\Delta E}{E_\gamma} = \frac{0.048 \text{ neV}}{14.41 \text{ keV}} \approx 10^{-15}$$

Hyperfine Interactions between Nuclei and Electrons ⇒ Mössbauer Parameters

Electric Monopole Interaction ⇒ Isomer Shift S ⇒ Electron density ρ



Electric Quadrupole Interaction ⇒ Quadrupole Splitting ⇒ Electric Field Gradient EFG



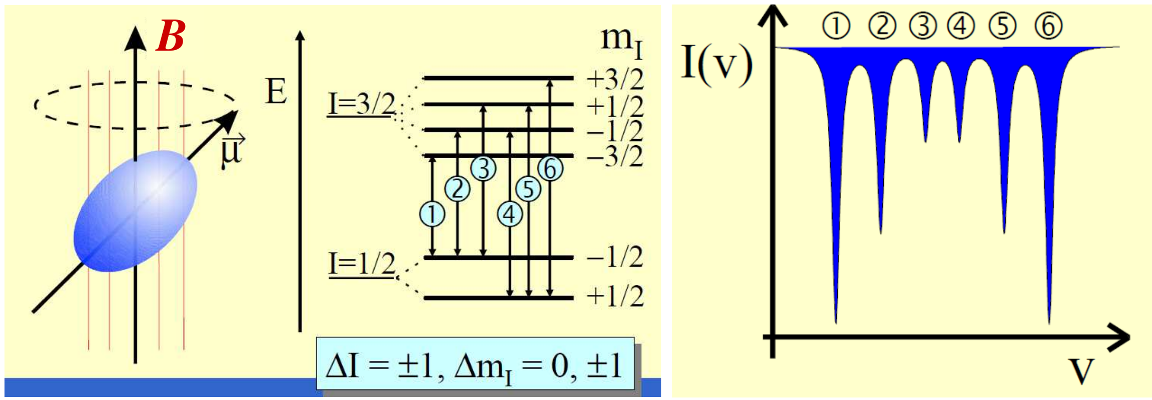
$\Delta S \rightarrow \Delta\rho$

1 mm/s → 3.4 el./Bohr^3

$\Delta E_Q \rightarrow$ EFG

1 mm/s → $5.7 \cdot 10^{21}$ V/m^2

Magnetic Dipole Interaction ⇒ Magnetic Splitting ⇒ Magnetic hyperfine field B



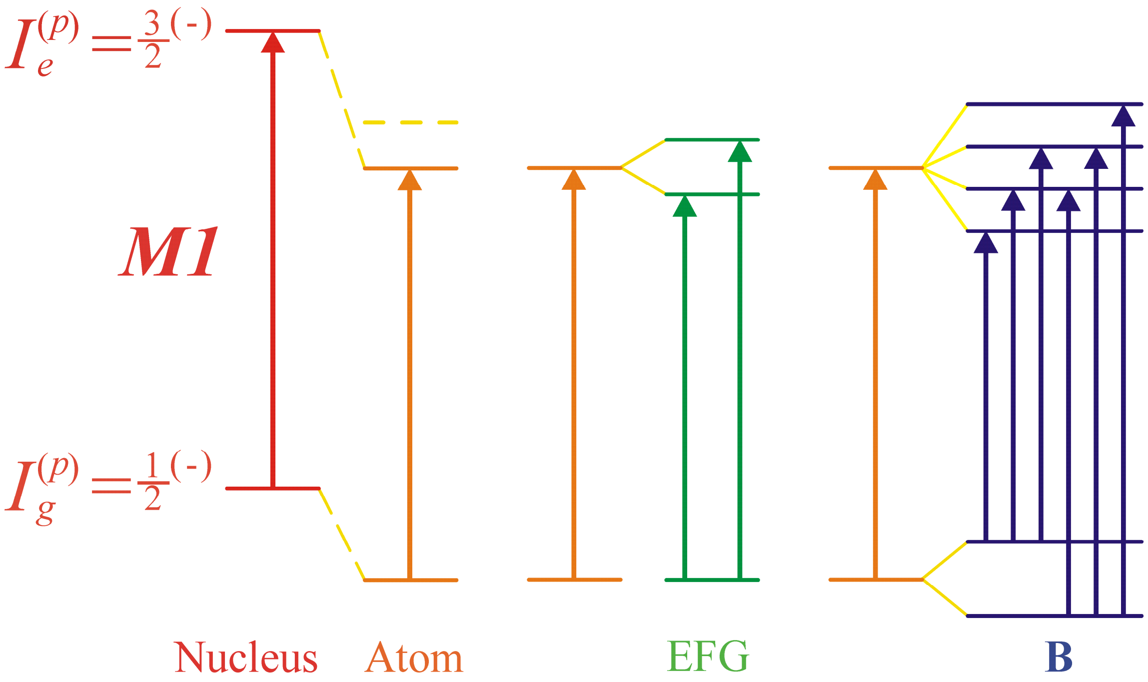
	B
α-Fe	→ 33 Tesla
Fe_2O_3	→ 52 Tesla
$BaFe_2As_2$	→ 5.3 Tesla

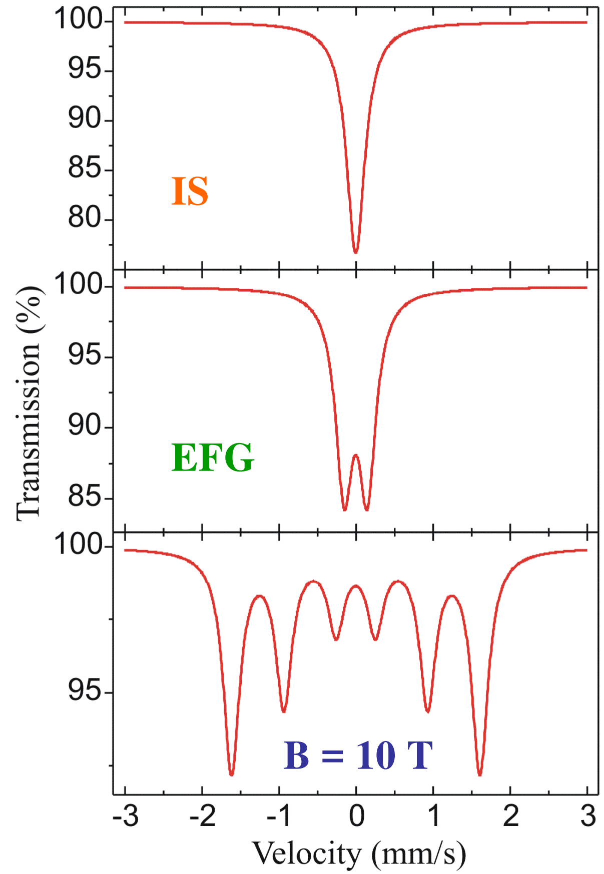
Hyperfine Interactions

Isomer Shift

Quadrupole Splitting

Magnetic Splitting



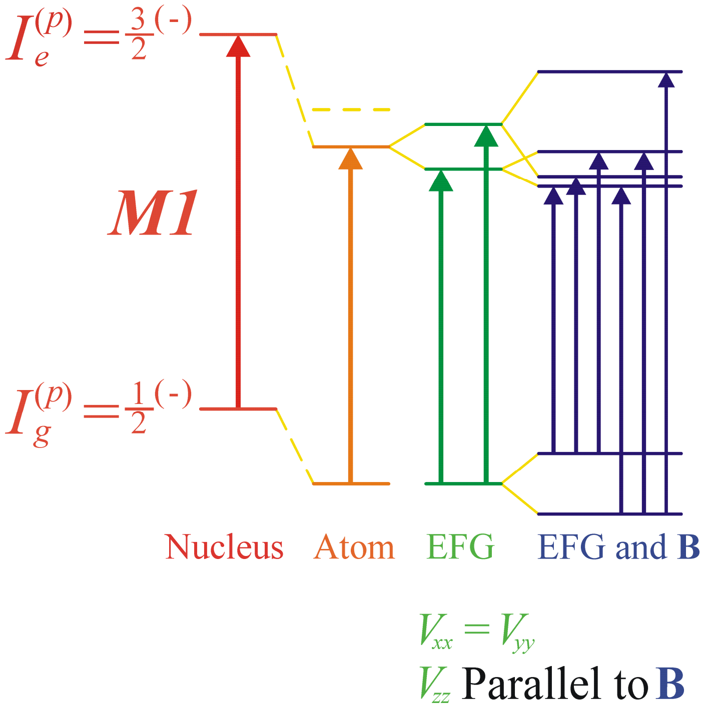


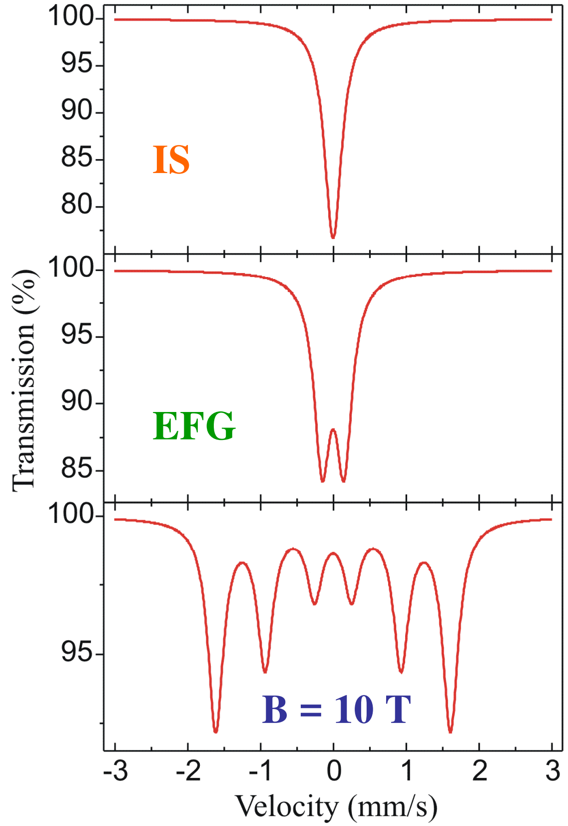
Electron Density

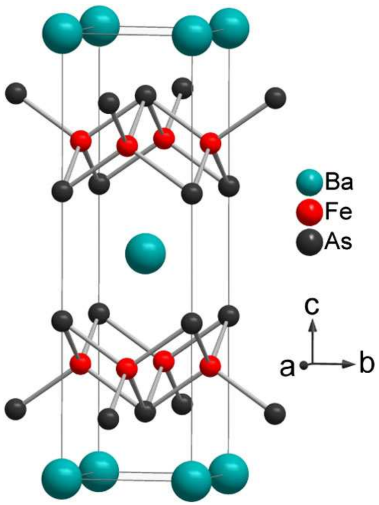
Electric Field Gradient

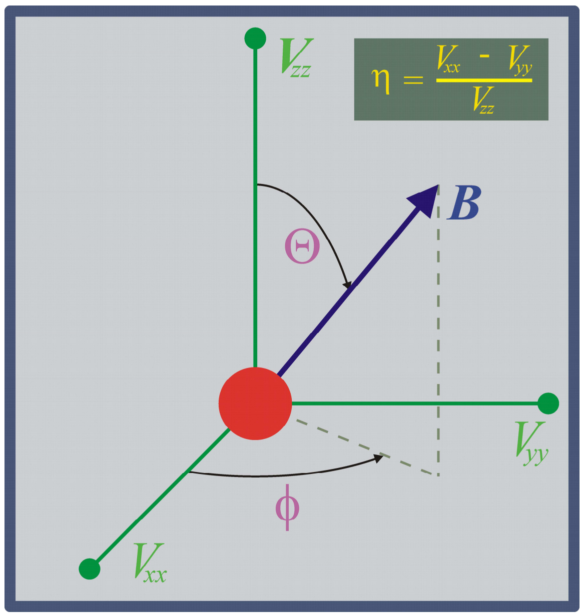
Magnetic Hyperfine Field

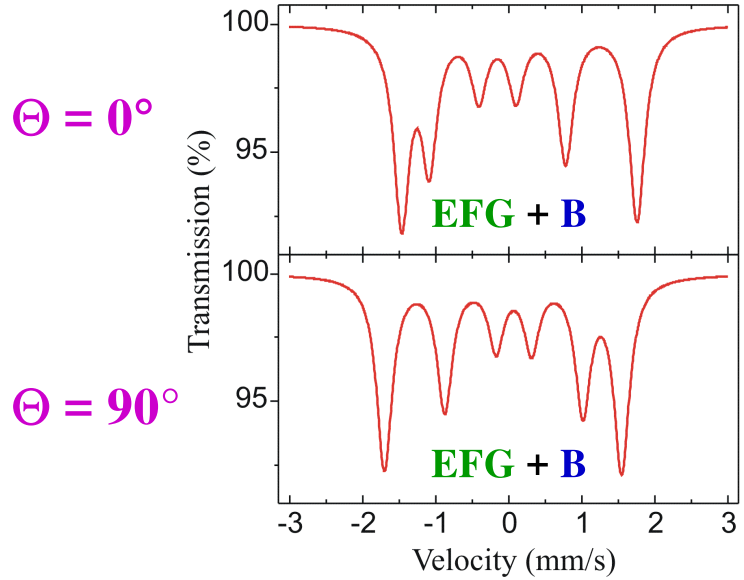
Electric Field Gradient + Magnetic Hyperfine Field



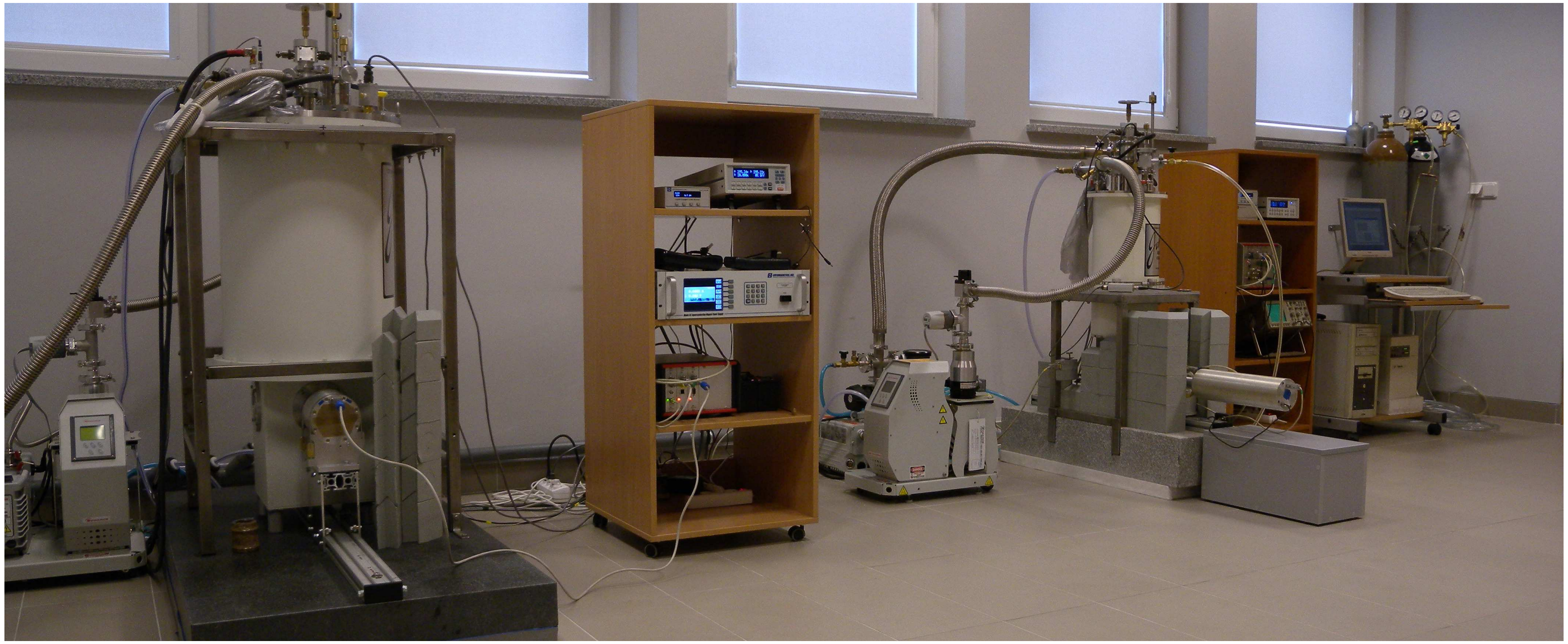


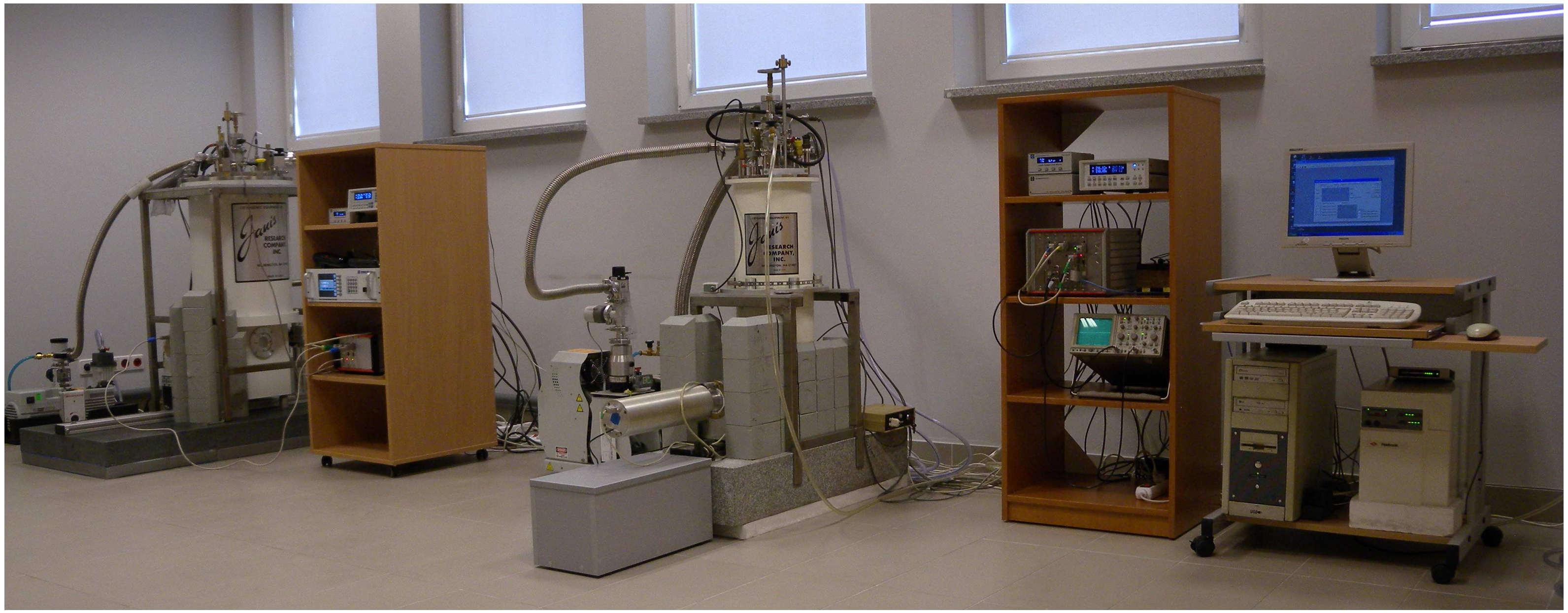






Mössbauer Spectroscopy Laboratory,
Pedagogical University, Kraków, Poland





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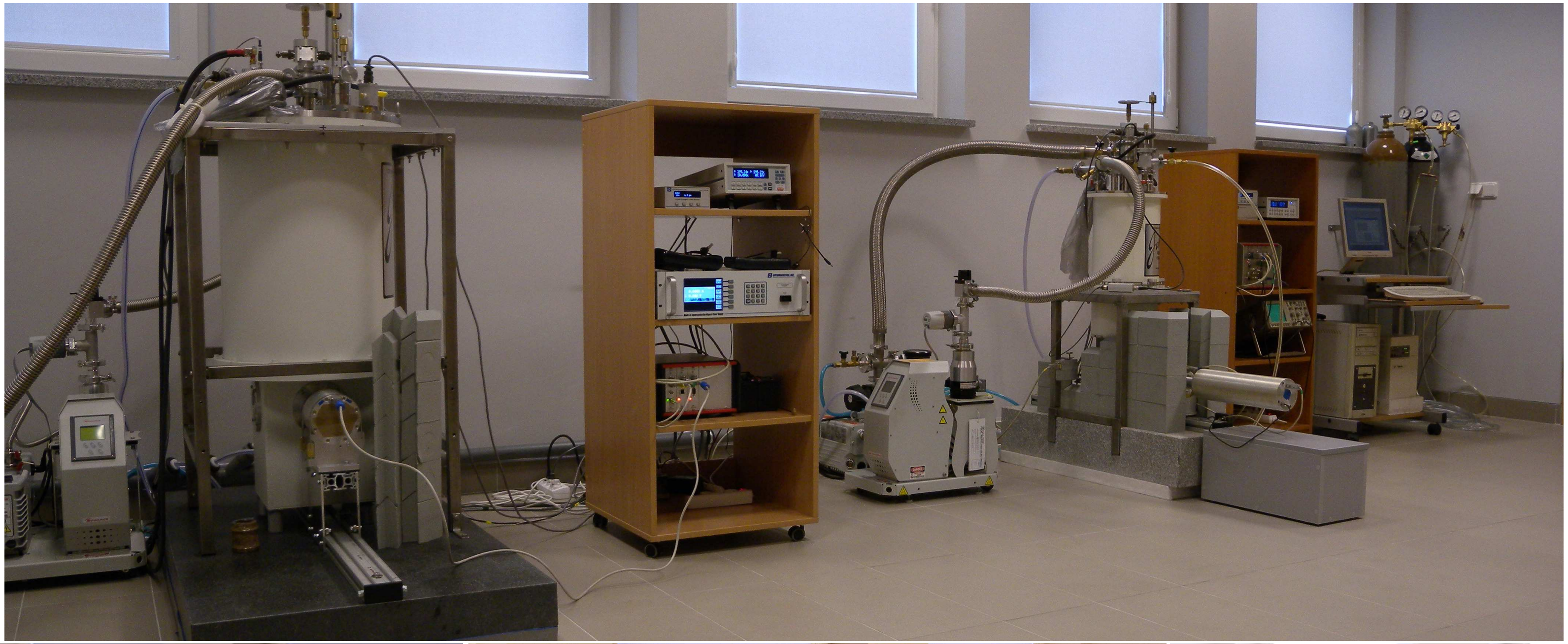
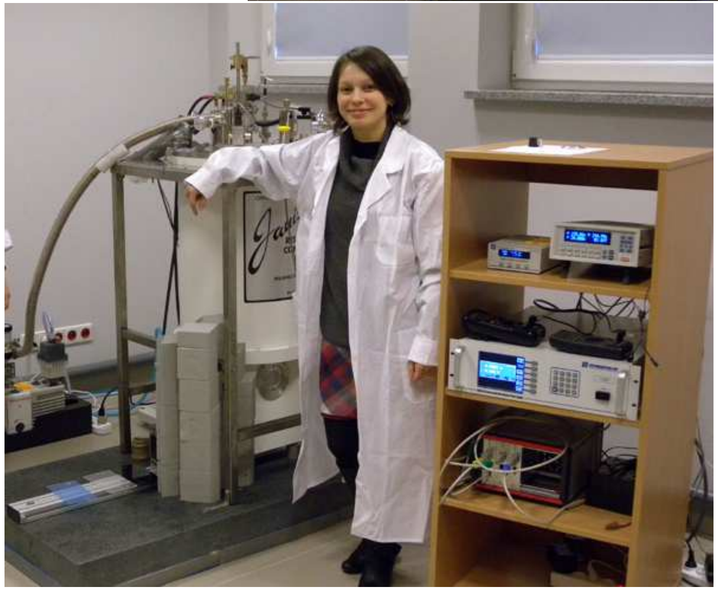
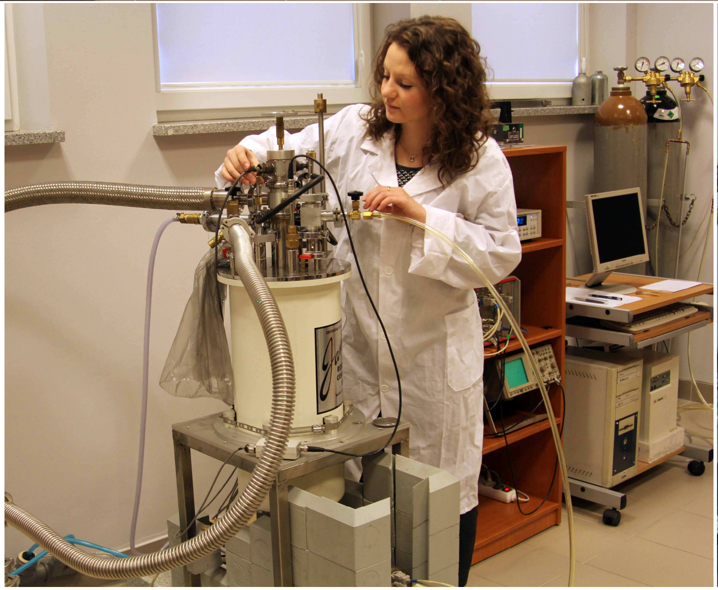


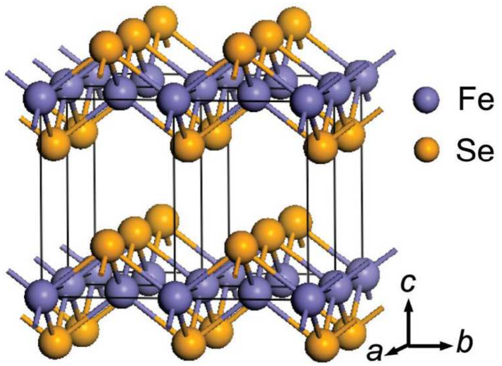


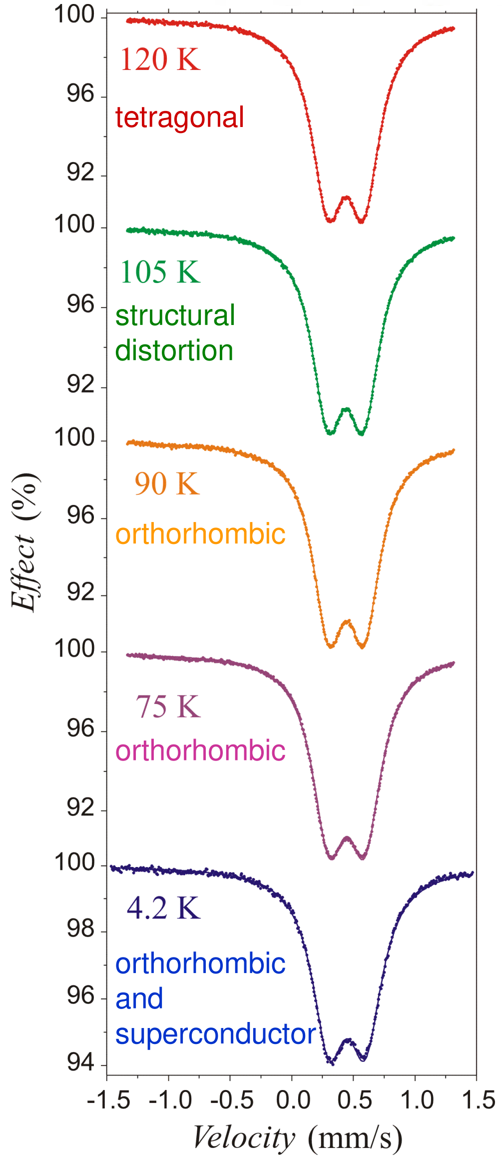
dr Aleksandra Jasek



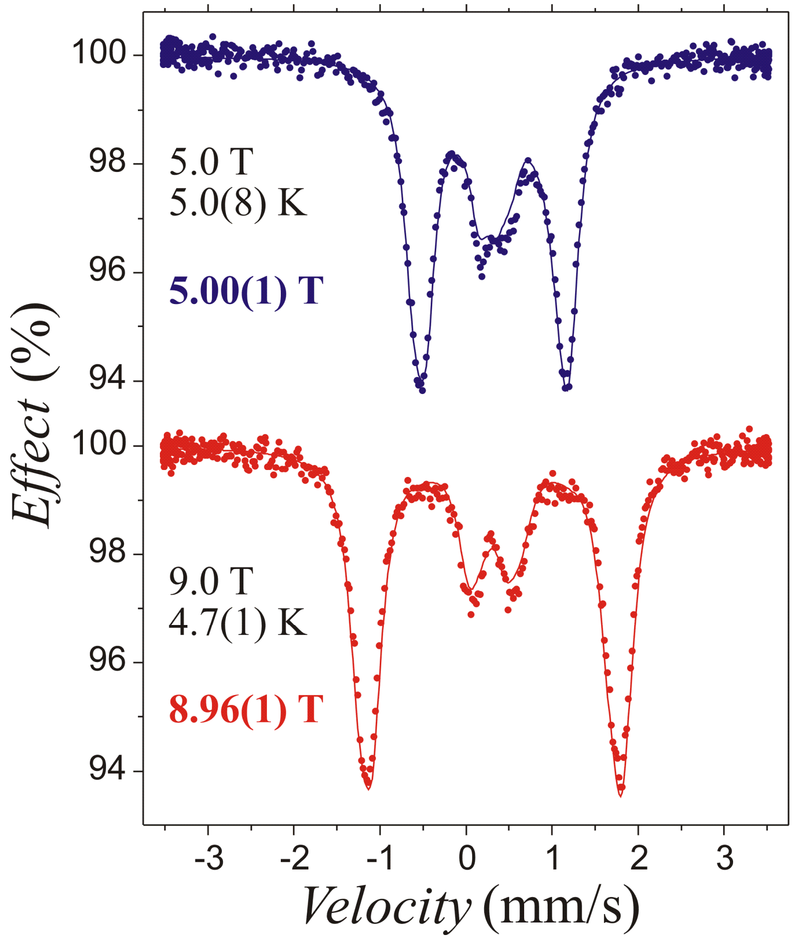
mgr Kamila Komędera
doktorantka

prof. Krzysztof Ruebenbauer





$Fe_{1.01}Se$ $T_{sc} = 8$ K



Hyperfine magnetic field is equal to applied external magnetic field

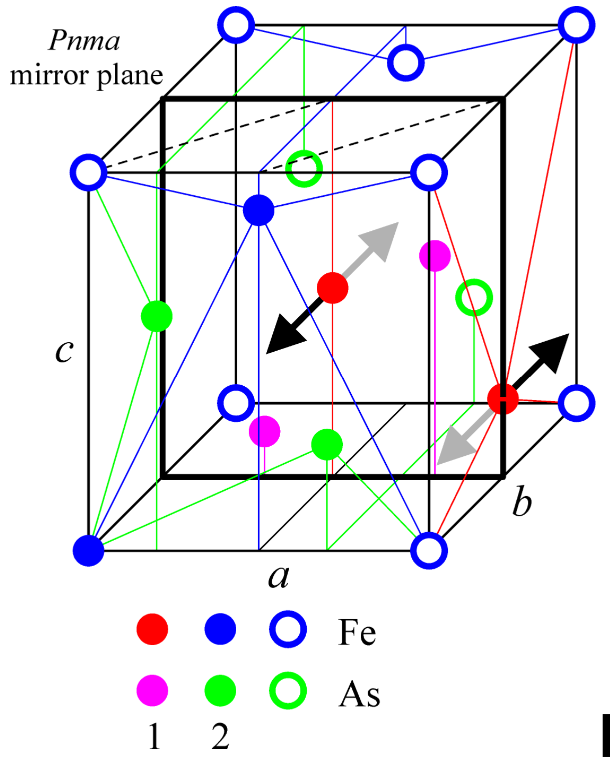
- it means that there is no magnetic moment on the Fe atoms

Mössbauer spectroscopy evidence for the lack of iron magnetic moment in superconducting FeSe

A.Błachowski, K.Ruebenbauer, J.Żukrowski, J.Przewoźnik, K.Wojciechowski, Z.M.Stadnik

JALLCOM **494**, 1 (2010)

Crystal structure of FeAs

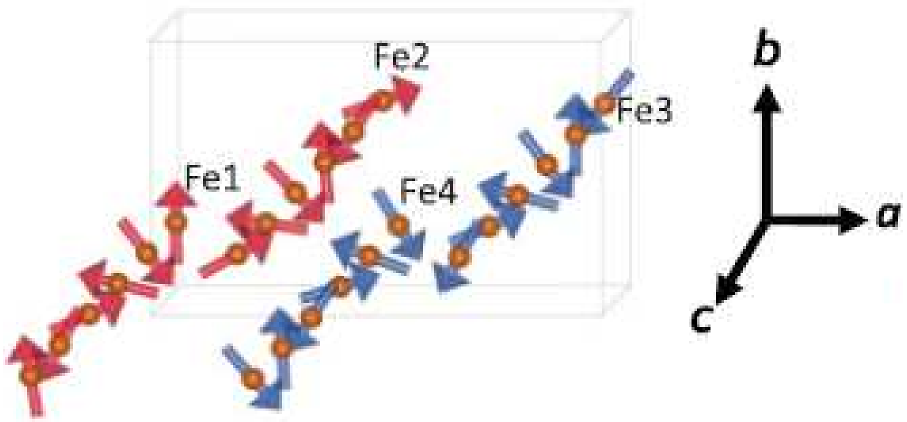


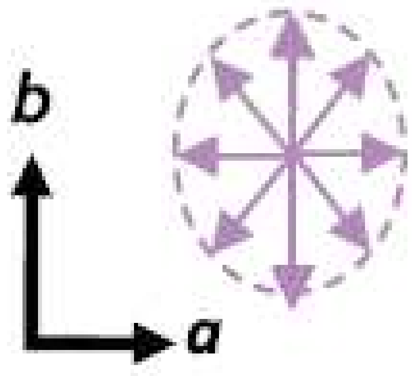
1. Orthorhombic structure
2. The *Pnma* symmetry group
3. Arrows show *Pna*2_1 distortion

[0 *k*+1/2 0] iron and [0 *k* 0] iron

Magnetic structure of FeAs

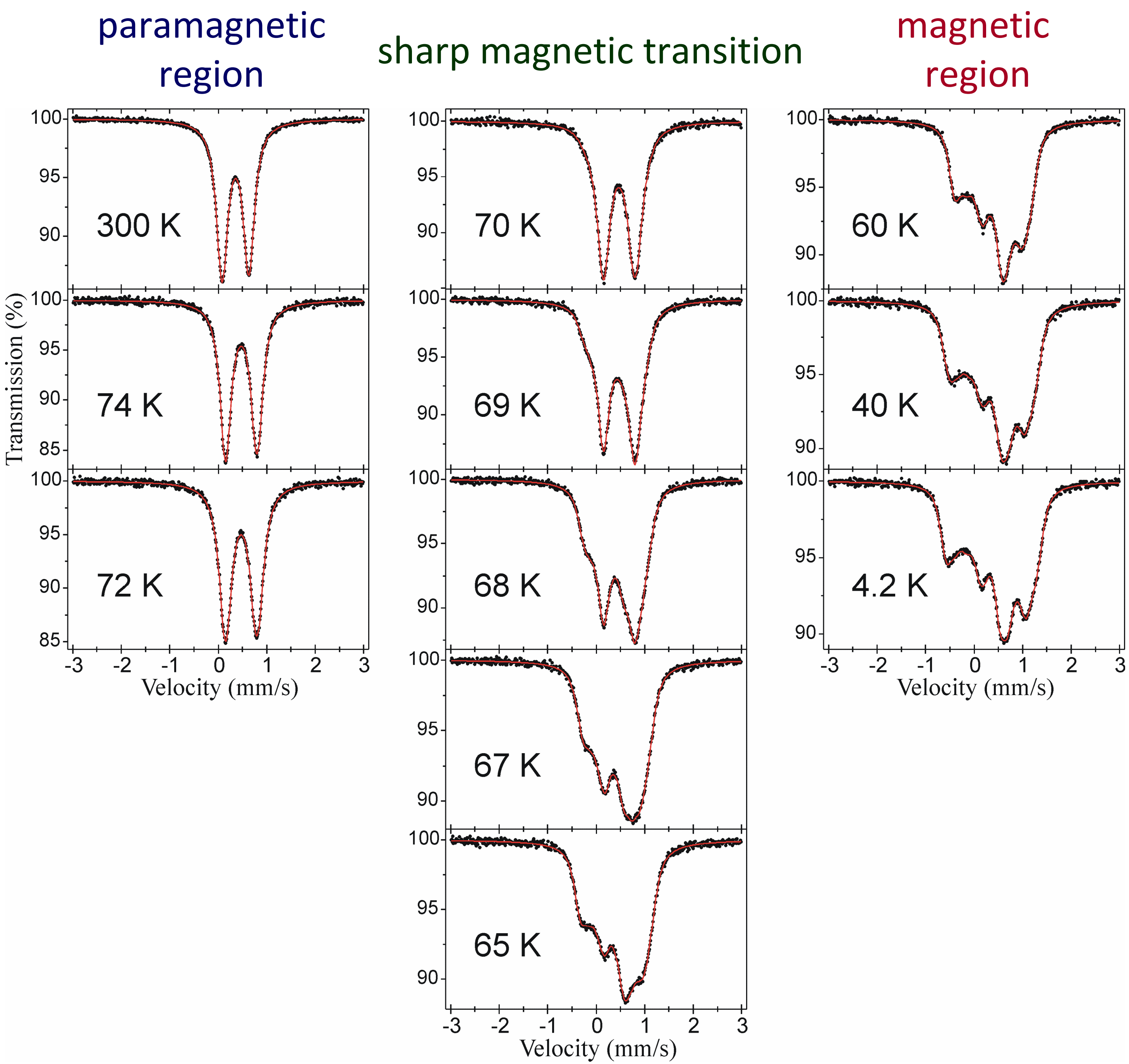
magnetic moments lay in a-b plane, make antiferromagnetic spirals propagating along the c-axis and incommensurate with the lattice period





Polarized neutron scattering results
E.E. Rodriguez *et al.*, PRB **83**, 134438 (2011)

FeAs

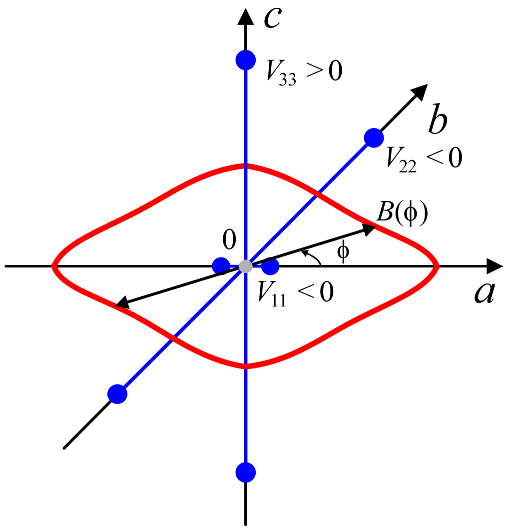


A.Błachowski, K.Ruebenbauer, J.Żukrowski, Z.Bukowski,
Magnetic anisotropy and lattice dynamics in FeAs studied by Mössbauer spectroscopy,
J. Alloys Compd. **582**, 167 (2014)

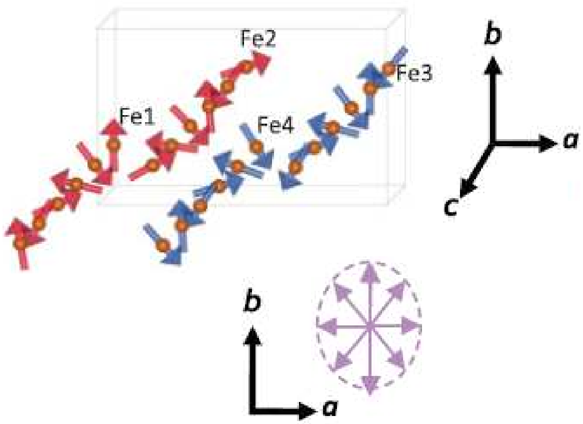
Anisotropy of the hyperfine magnetic fields (spiral projections onto *a*-*b* plane) in FeAs

Left column shows [0 *k*+1/2 0] iron, right column shows [0 *k* 0] iron.

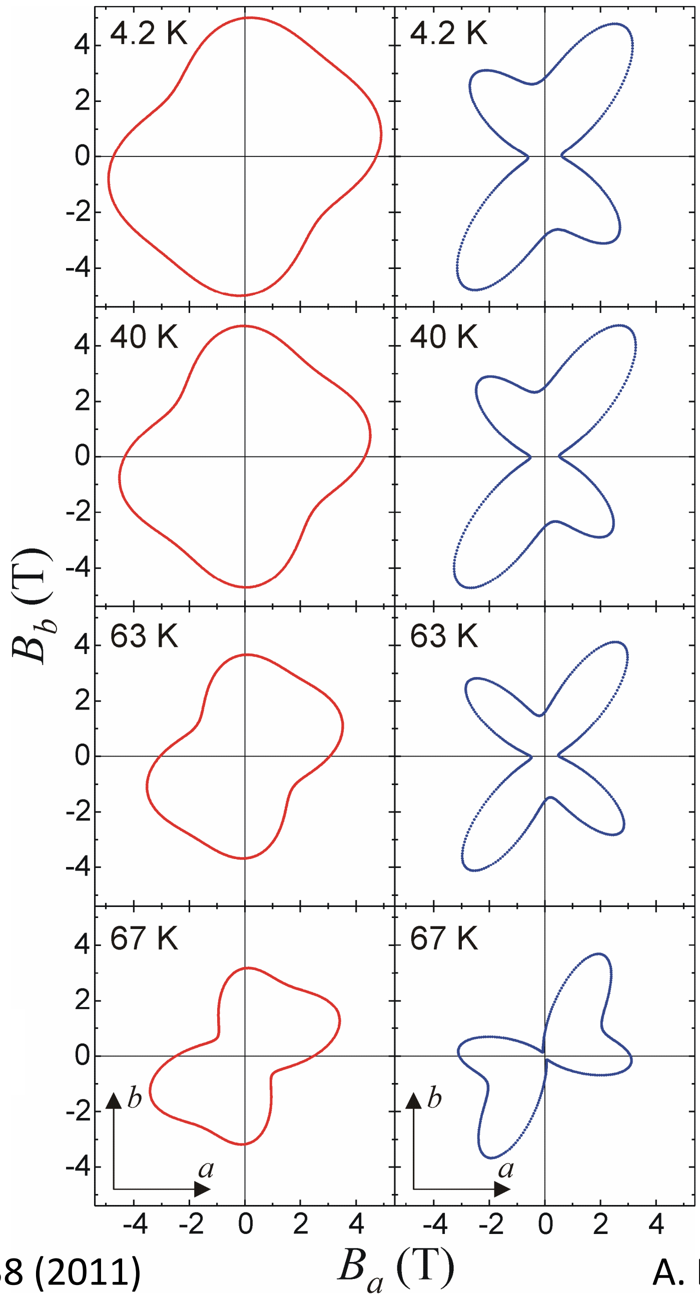
B_a and B_b - iron hyperfine field components along the *a*-axis and *b*-axis, respectively.

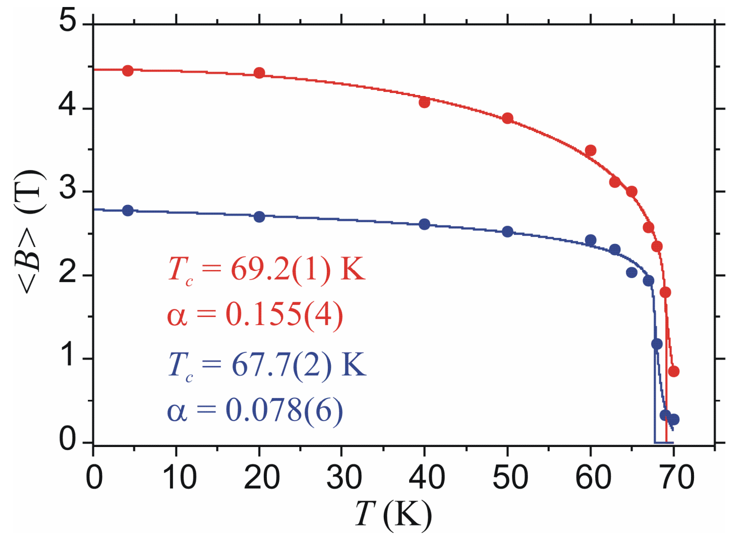


Orientation of the EFG
and
hyperfine magnetic field
in the main crystal axes



E.E. Rodriguez *et al.*, PRB 83, 134438 (2011)





Average hyperfine fields <*B*>
for
[0 *k*+1/2 0] and [0 *k* 0] irons.

T_c - transition temperature
α - static critical exponent

A. Błachowski *et al.*, JALLCOM **582**, 167 (2014)

"122" Fe-based Superconducting Family

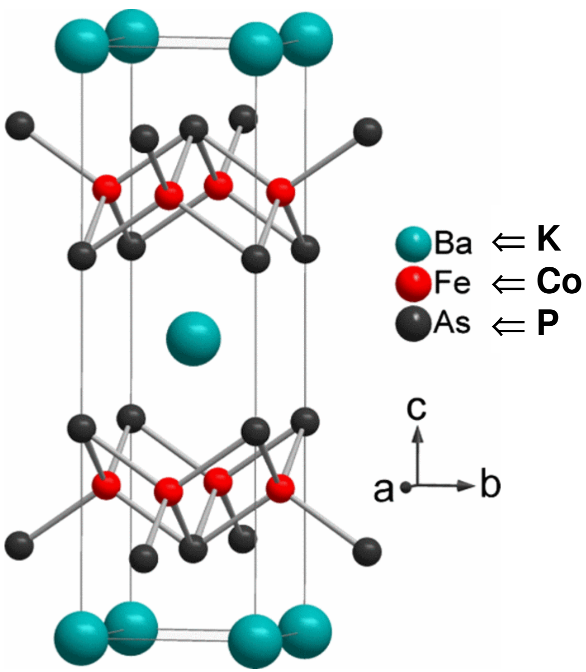
AFe_2As_2 (A = Ca, Sr, Ba, Eu)

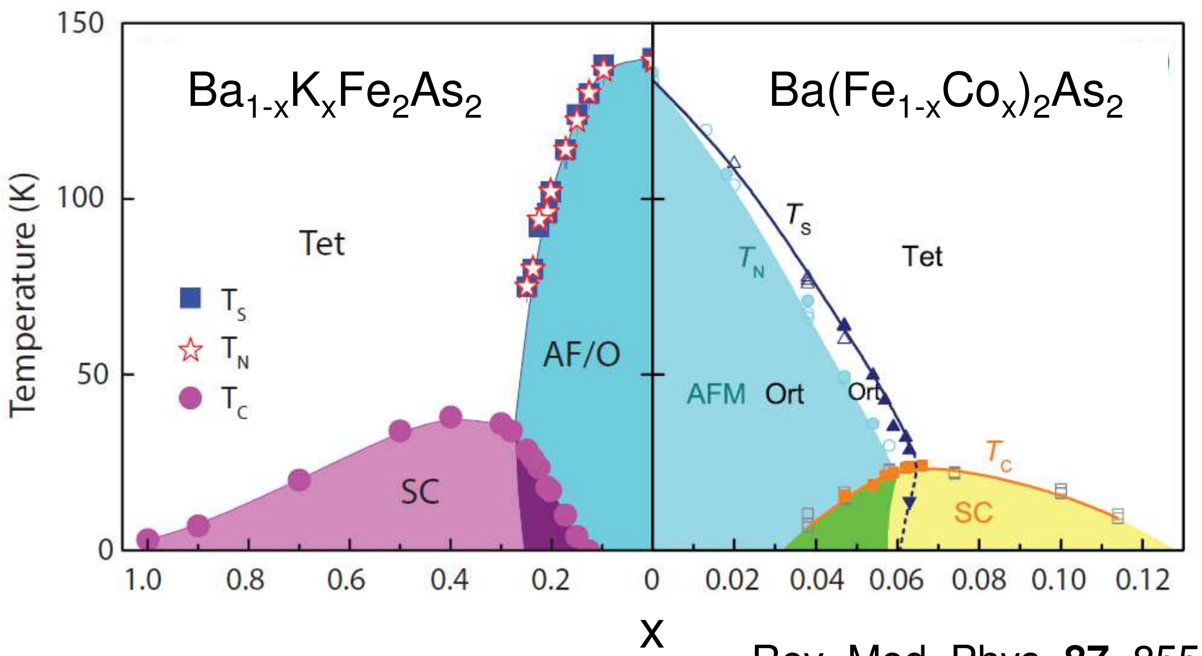
Parent compound

$BaFe_2As_2$ T_{SDW} = 136 K

Superconductors

$Ba_{1-x}K_xFe_2As_2$	$Ba(Fe_{1-x}Co_x)_2As_2$	$BaFe_2(As_{1-x}P_x)_2$
hole-doping	electron-doping	isovalent-substitution
x = 0.40	x = 0.08	x = 0.31
T_{sc} = 38 K	T_{sc} = 24 K	T_{sc} = 31 K



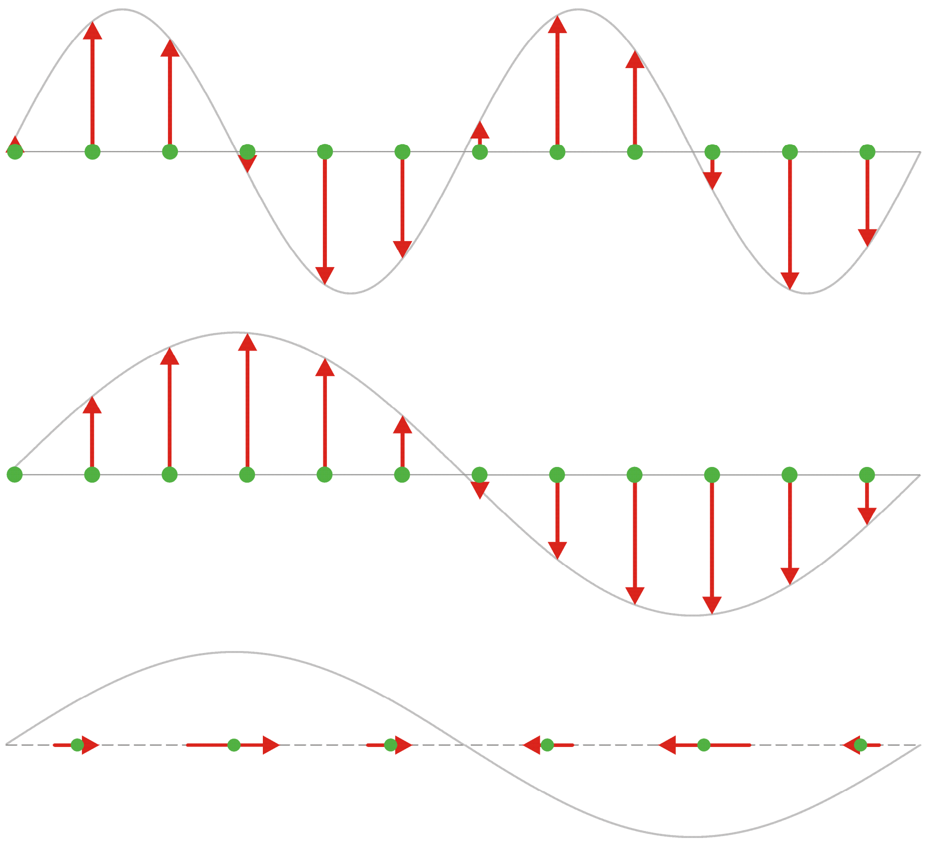


Rev. Mod. Phys. **87**, 855 (2015)

Charge density wave (CDW) - spatial modulation of the electron charge density

Electric field gradient wave (EFGW) - spatial modulation of the electric field gradient

Spin density wave (SDW) - spatial modulation of the electron spin density



Modulations (waves) :

- perpendicular or longitudinal ?
- commensurate or incommensurate ?

The Mössbauer spectroscopy is sensitive
to the spin and charge (electron) distribution around the resonant atoms
via the hyperfine magnetic field, isomer shift and electric quadrupole interaction.

Spin density wave (SDW) as seen by Mössbauer Spectroscopy

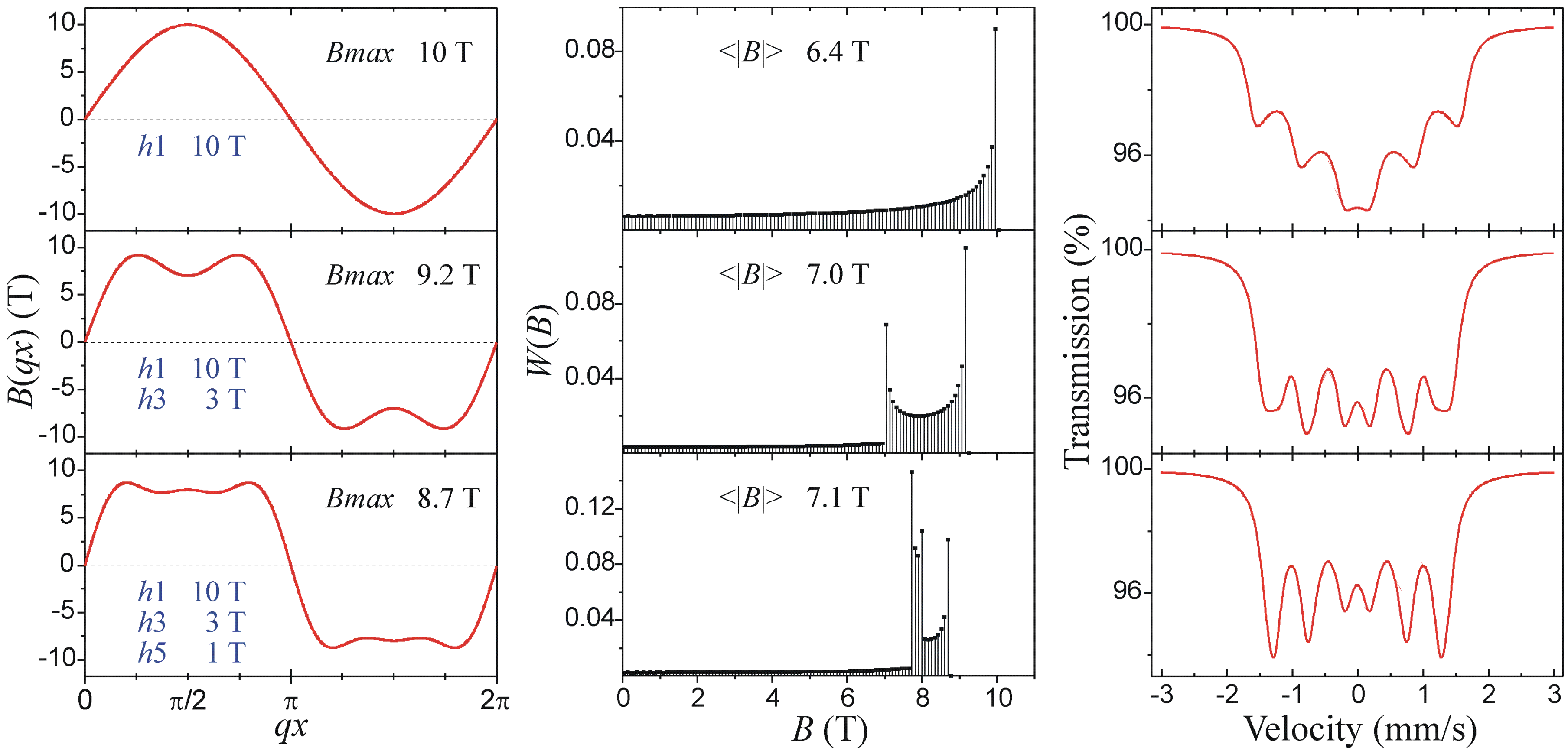
$$B(qx) = \sum_{n=1}^{N} h_{2n-1} \sin[\,(2n-1)\,qx\,]$$

$h_{2n\text{-}1}$ – amplitudes of subsequent harmonics

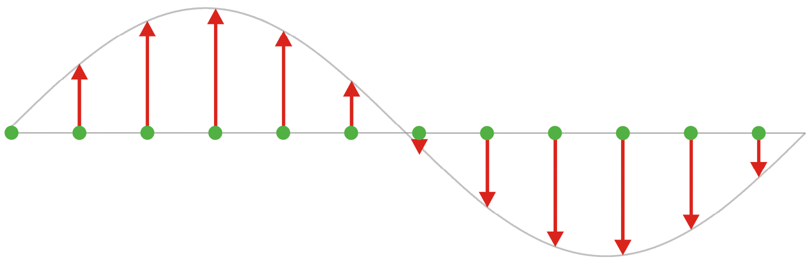
q – wave number of SDW

x – relative position of the resonant nucleus along propagation direction of SDW

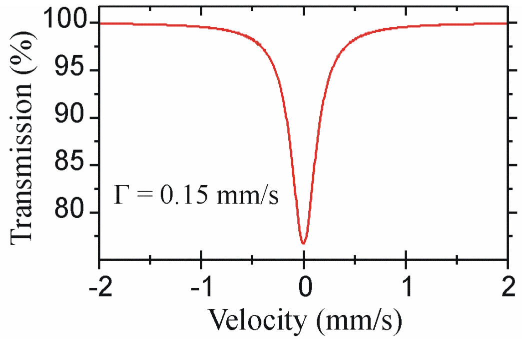
SDW | hyperfine field distribution | ^{57}Fe Mössbauer spectrum

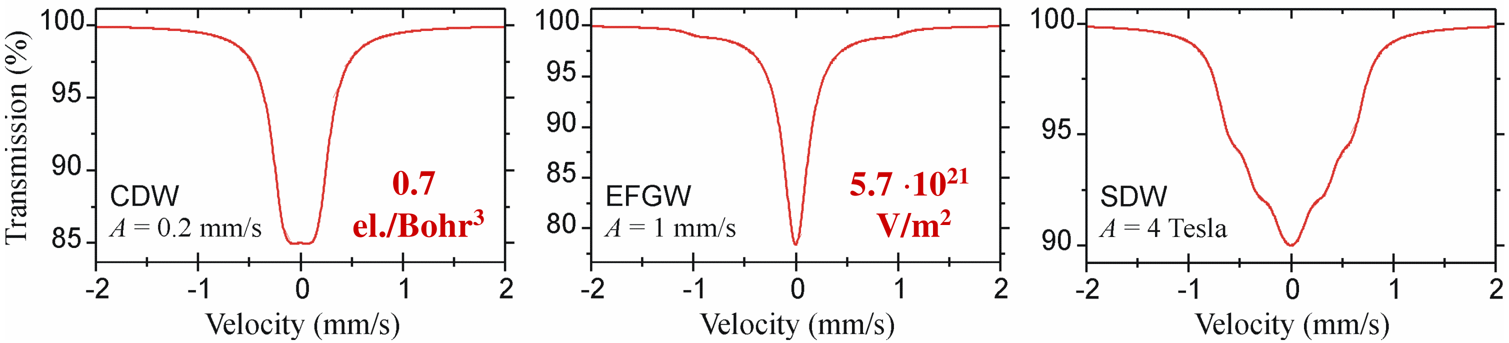


CDW , EFGW and SDW as seen by Mössbauer Spectroscopy



Γ – absorber line width





Charge and spin density modulations causes specific broadening of the Mössbauer absorption line.

For CDW one can estimate dispersion (around average value) of the electron density $\Delta\rho$

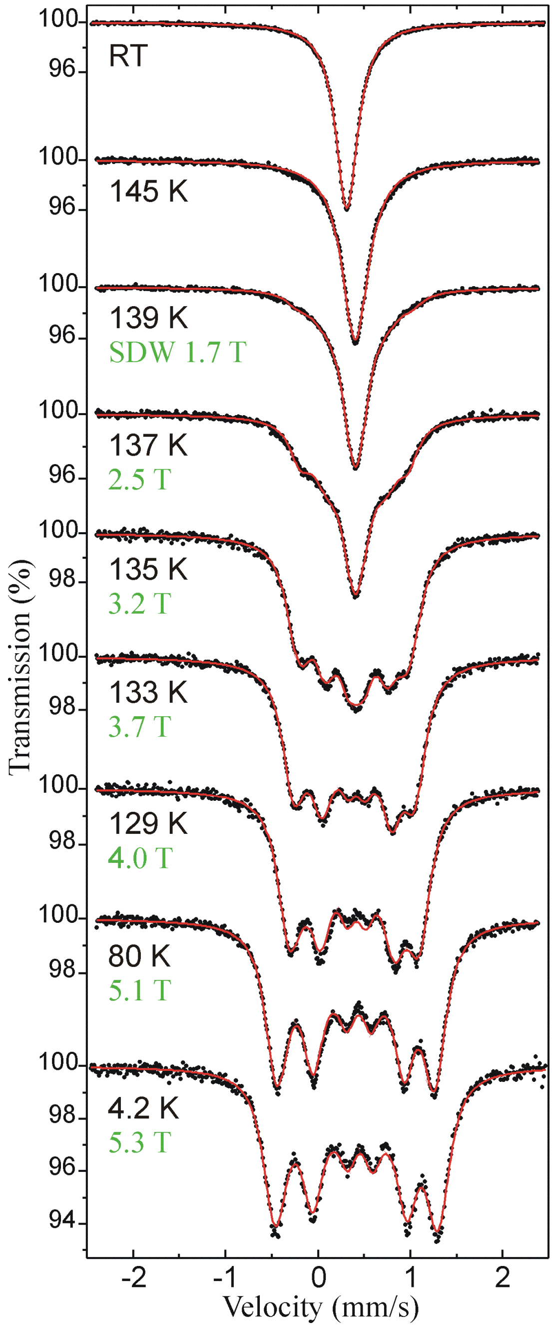
$$\Delta\rho = \sqrt{(\Gamma^2 - \Gamma_0^2)/\alpha^2}$$

$\Gamma_0 = 0.1\,\text{mm/s}$ – unbroadened line width

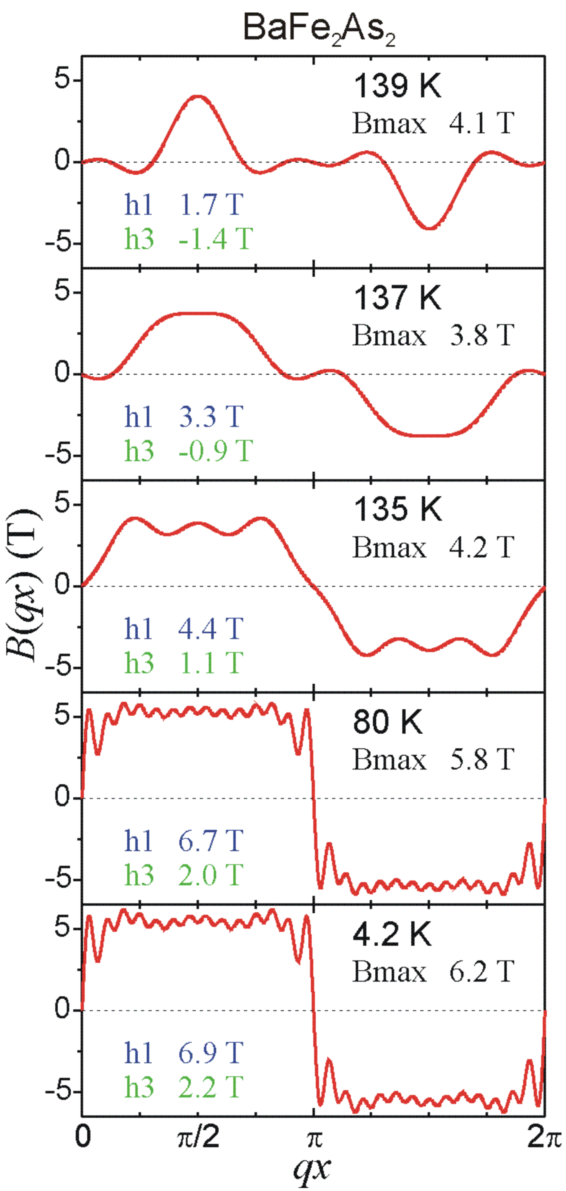
$\alpha = -0.291\,(\text{mm/s})\,(\text{Bohr})^3\,\text{el.}^{-1}$ – calibration constant

^{57}Fe Mössbauer spectra

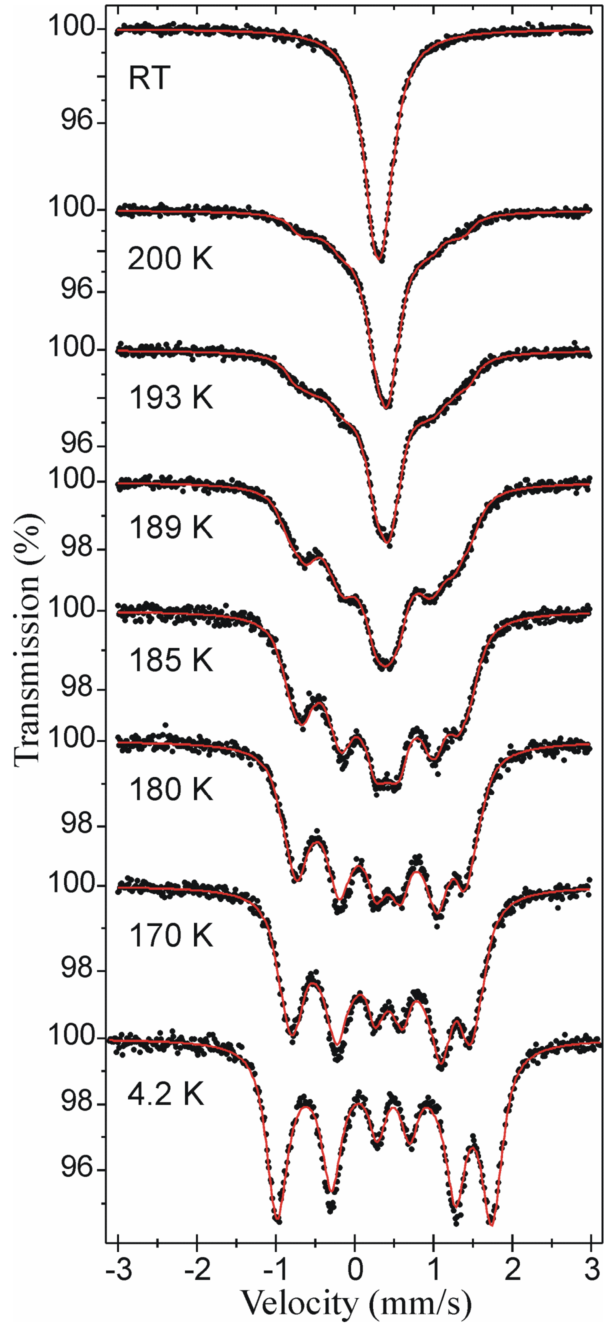
$BaFe_2As_2$
T_{SDW} = 136 K



Shape of SDW



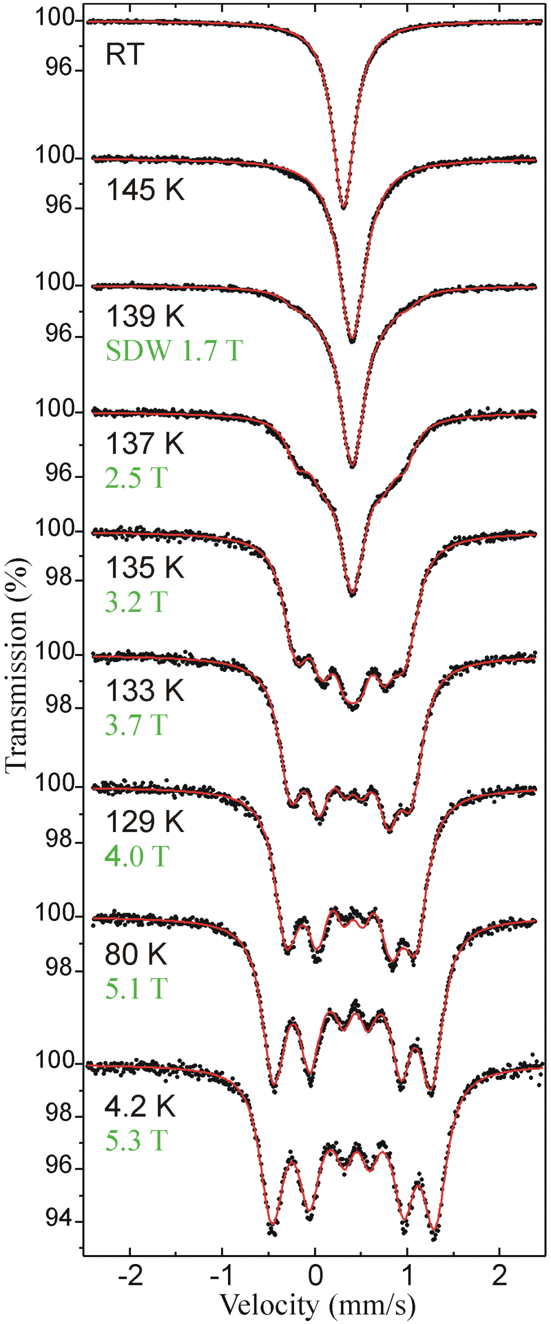
$EuFe_2As_2$
T_{SDW} = 192 K



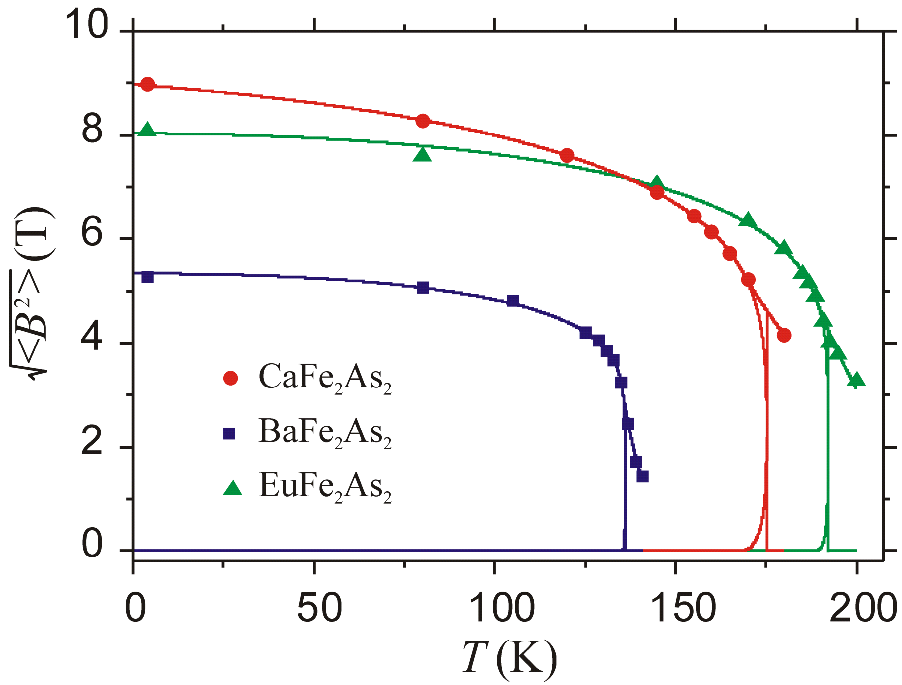
^{57}Fe Mössbauer spectra

$BaFe_2As_2$

$T_{SDW} = 136$ K



Root mean square amplitude of SDW



Compound	$CaFe_2As_2$	$BaFe_2As_2$	$EuFe_2As_2$
T_c (K)	175.3(3)	136.0(1)	192.1(1)
α_0	**0.158(2)**	**0.102(1)**	**0.124(1)**

critical exponent $\alpha_0 \approx 0.125$ ⇒ universality class (1, 2)

↓

one dimension in the spin space (Ising model)

and

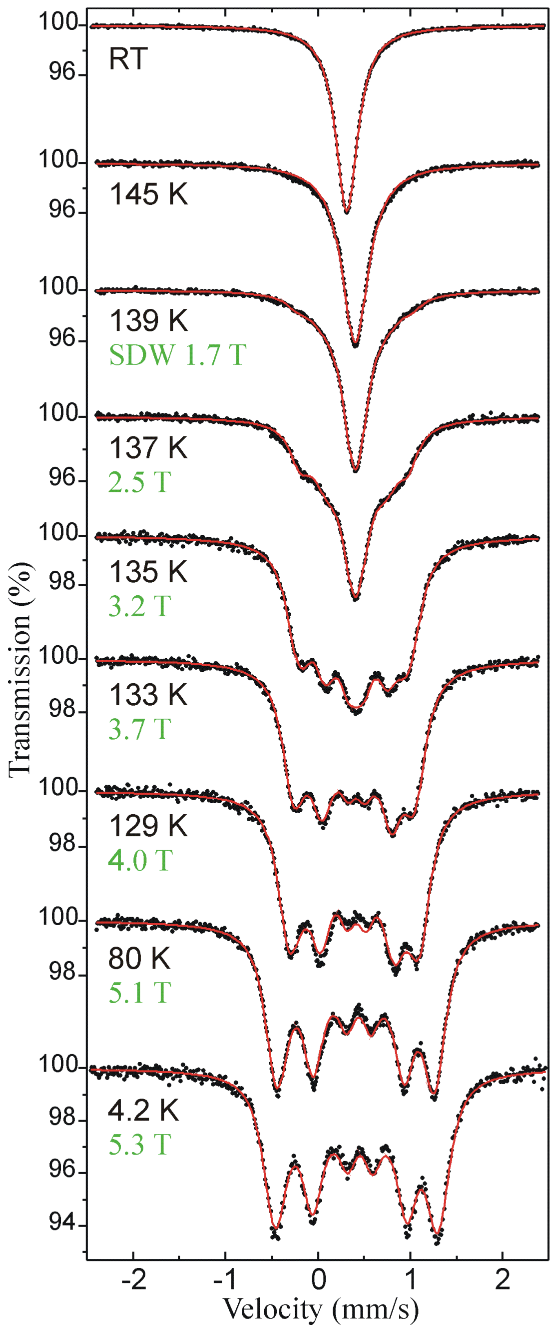
two dimensions in the real space (magnetic planes)

A.Błachowski, K.Ruebenbauer, J.Żukrowski, K.Rogacki, Z.Bukowski, J.Karpinski, Shape of spin density wave versus temperature in AFe_2As_2 (A = Ca, Ba, Eu) Phys. Rev. B **83**, 134410 (2011)

^{57}Fe Mössbauer spectra

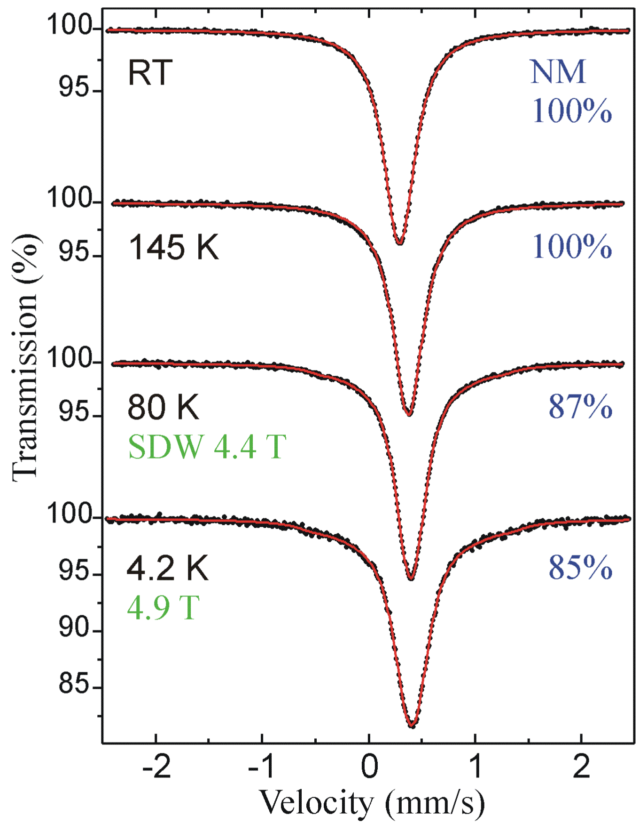
$BaFe_2As_2$ *(parent)*

$T_{SDW} = 136$ K



$Ba_{0.7}Rb_{0.3}Fe_2As_2$ *(superconductor)*

$T_{sc} = 37$ K

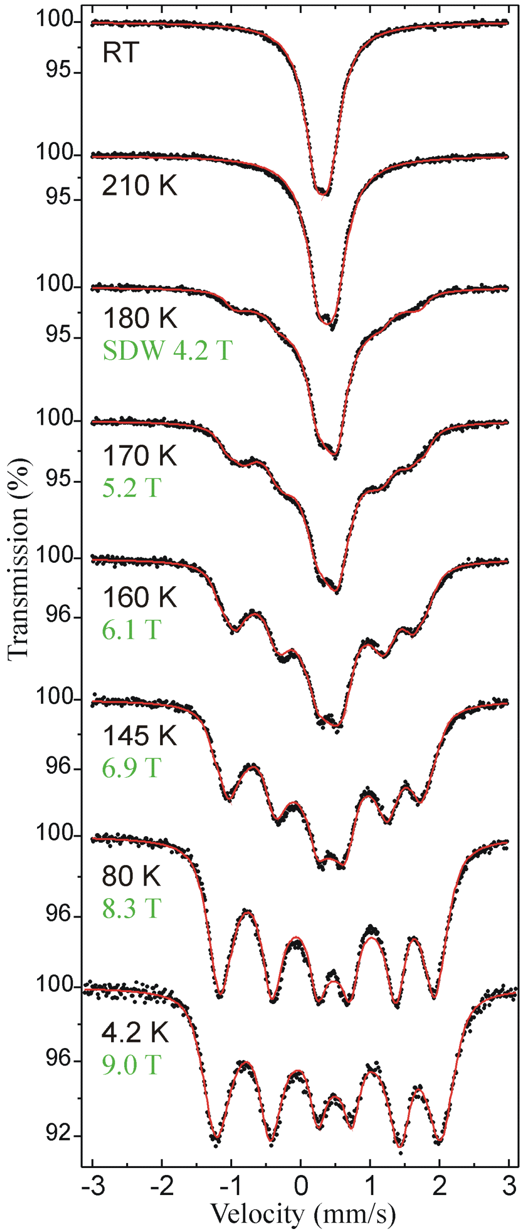


SDW is suppressed by doping

A.Błachowski, K.Ruebenbauer, J.Żukrowski, Z.Bukowski, M.Matusiak, J.Karpinski,
Interplay between spin density wave and superconductivity in '122' iron pnictides
Acta Phys. Pol. A **121**, 726 (2012)

$CaFe_2As_2$ *(parent)*

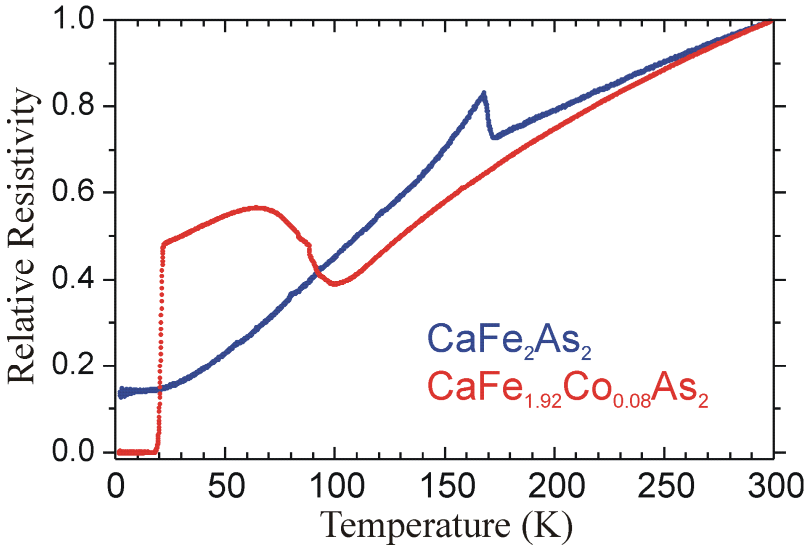
$T_{SDW} = 175$ K



Resistivity measurements:

It seems that

magnetism and superconductivity coexist (**?**).



Mössbauer measurements:

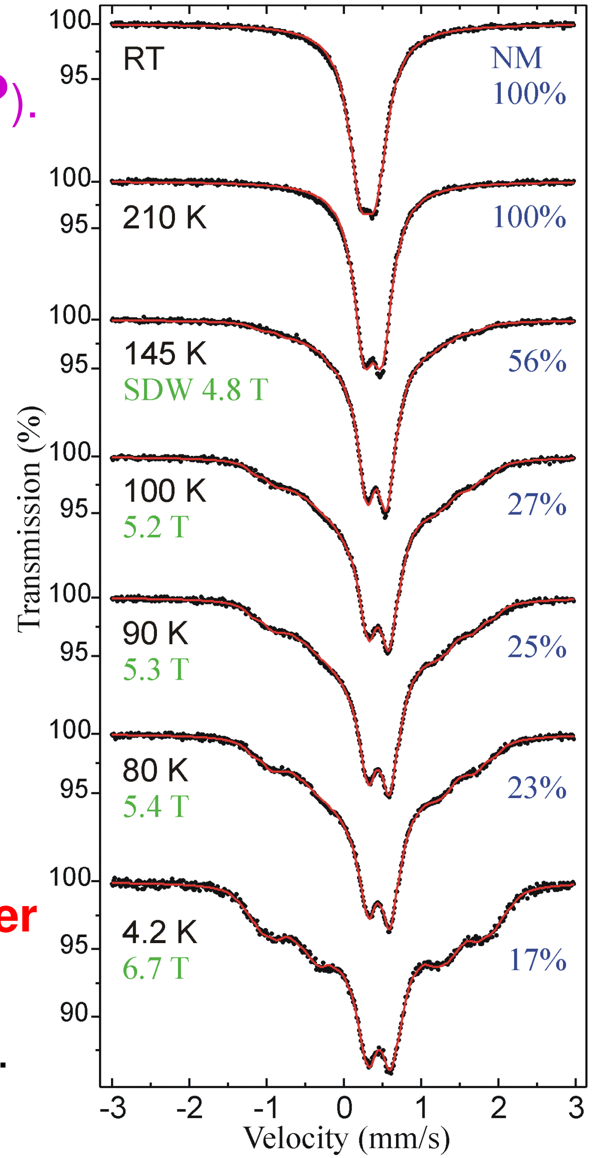
Superconductivity has **filamentary character** and occurs

in the regions free of **3d** magnetic moments.

$CaFe_{1.92}Co_{0.08}As_2$

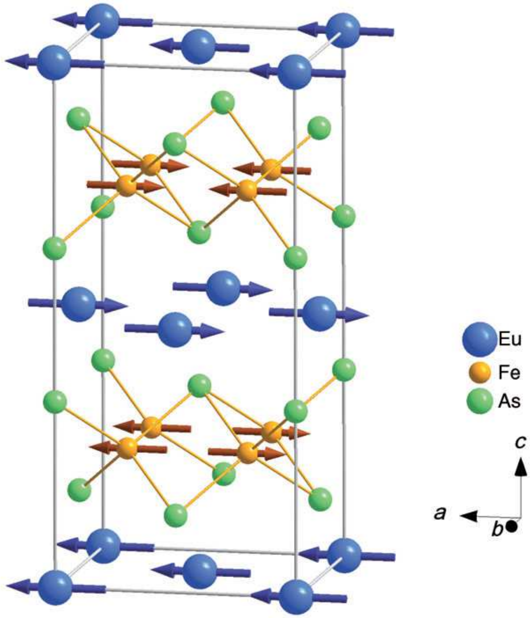
(superconductor)

$T_{sc} = 20$ K



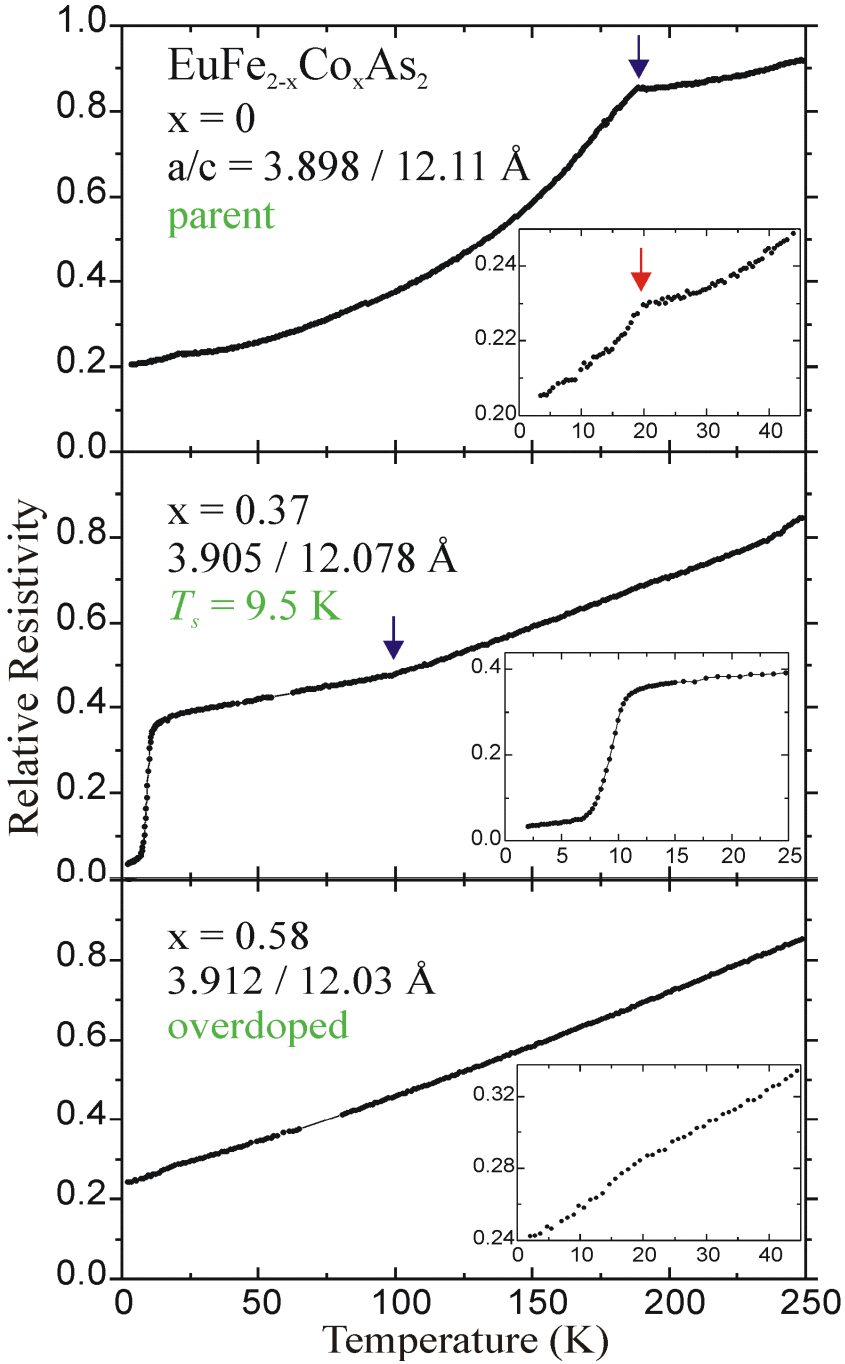
$EuFe_2As_2$

parent compound



T_{SDW} (Fe) = 192 K

T_N (Eu) = 19 K

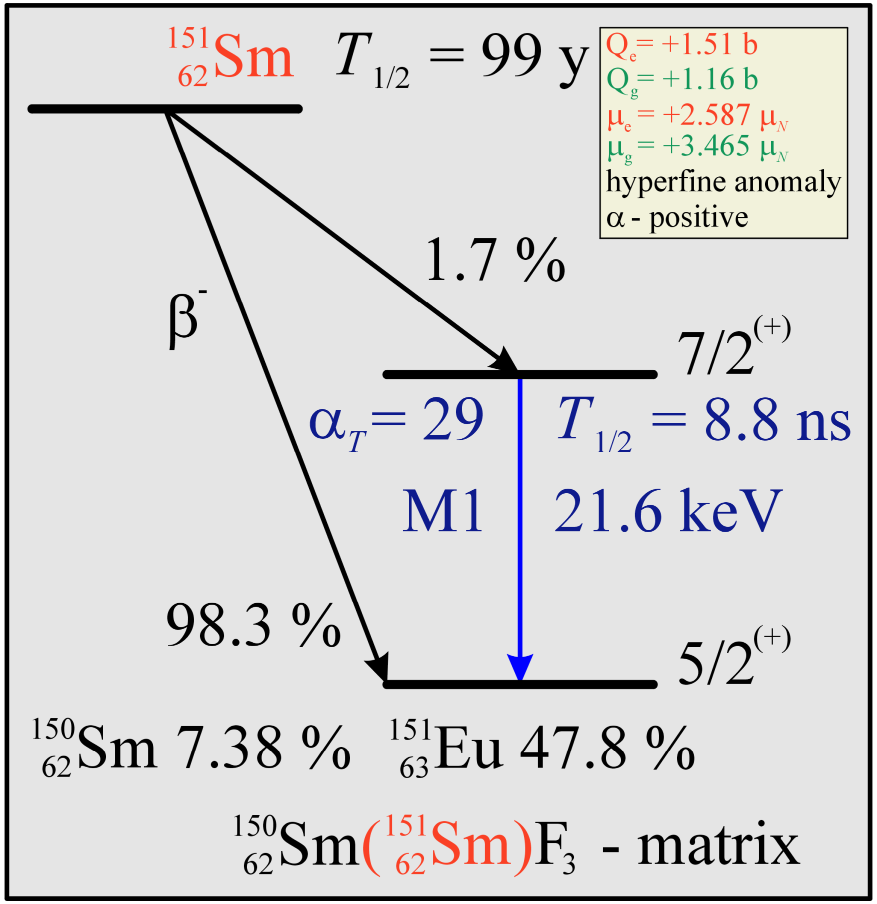


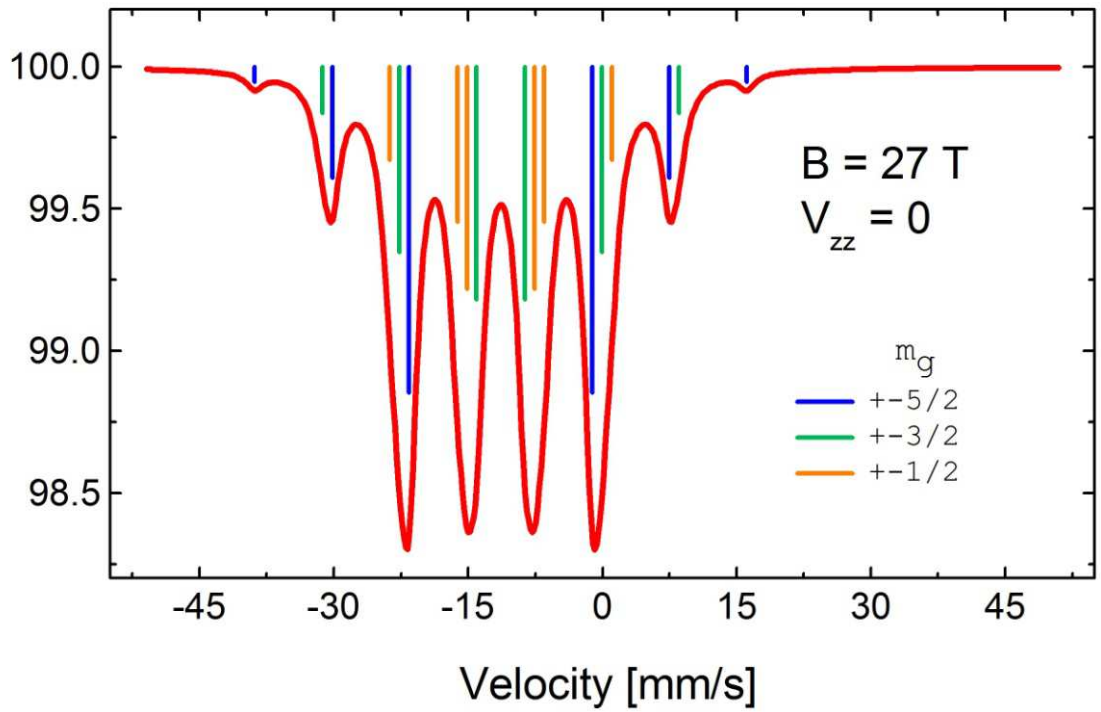
$EuFe_{2-x}Co_xAs_2$

superconductor

A.Błachowski, K.Ruebenbauer, J.Żukrowski, Z.Bukowski, K.Rogacki, P.J.W.Moll, J.Karpinski,
Interplay between magnetism and superconductivity in $EuFe_{2-x}Co_xAs_2$ studied by ^{57}Fe and ^{151}Eu Mössbauer spectroscopy,
Phys. Rev. B **84**, 174503 (2011)

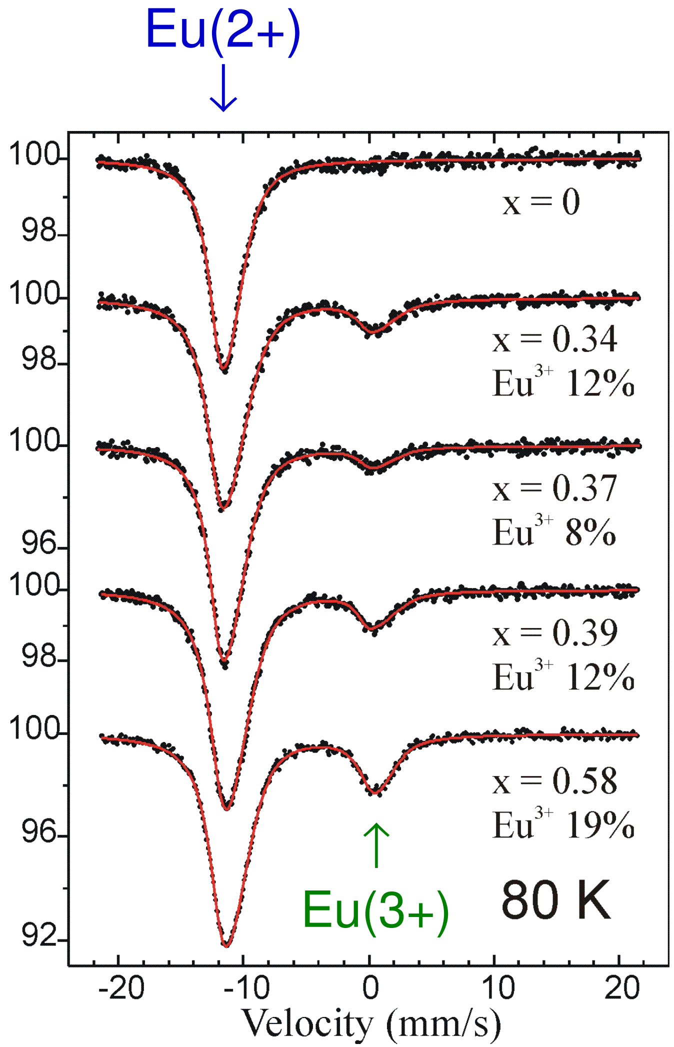
^{151}Eu Mössbauer spectroscopy

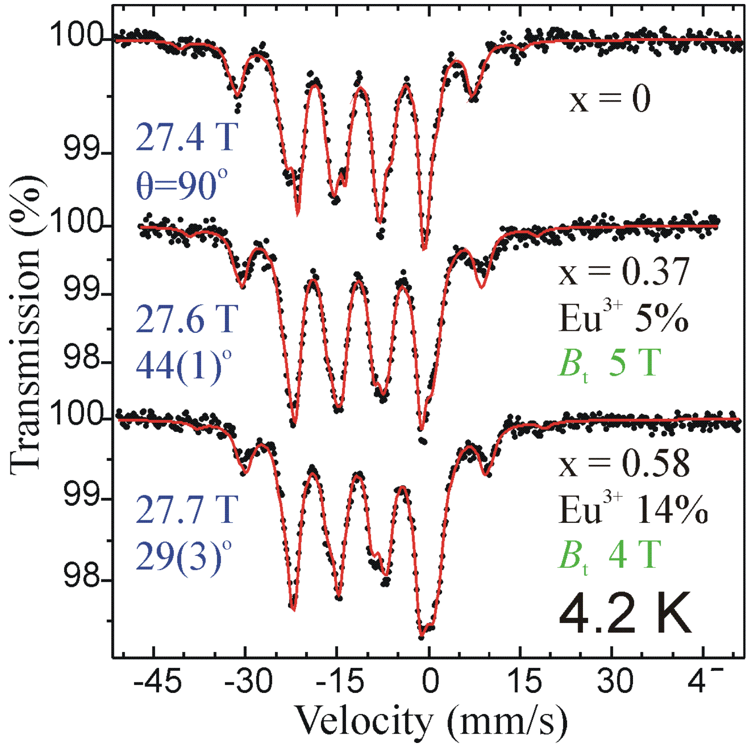




$EuFe_{2-x}Co_xAs_2$

^{151}Eu Mössbauer spectra



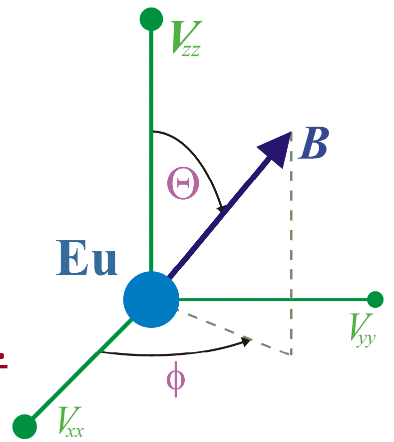


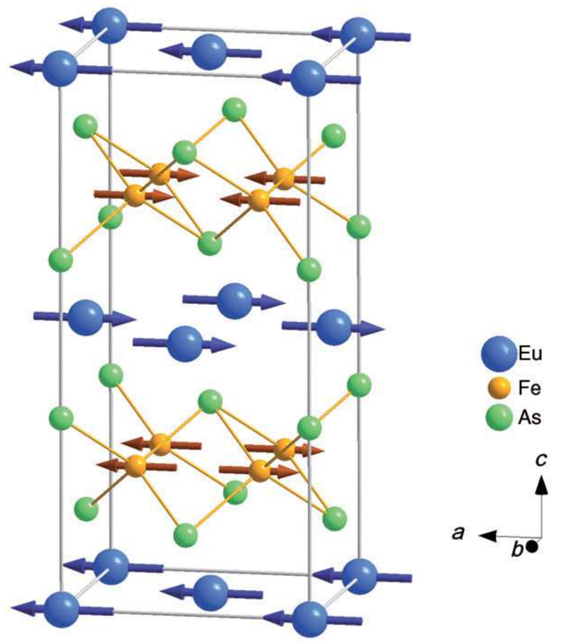
← Parent

← Superconductor

T_{sc} = 9.5 K

← Over-doped





Eu^{2+} orders magnetically regardless of the Co-substitution level.

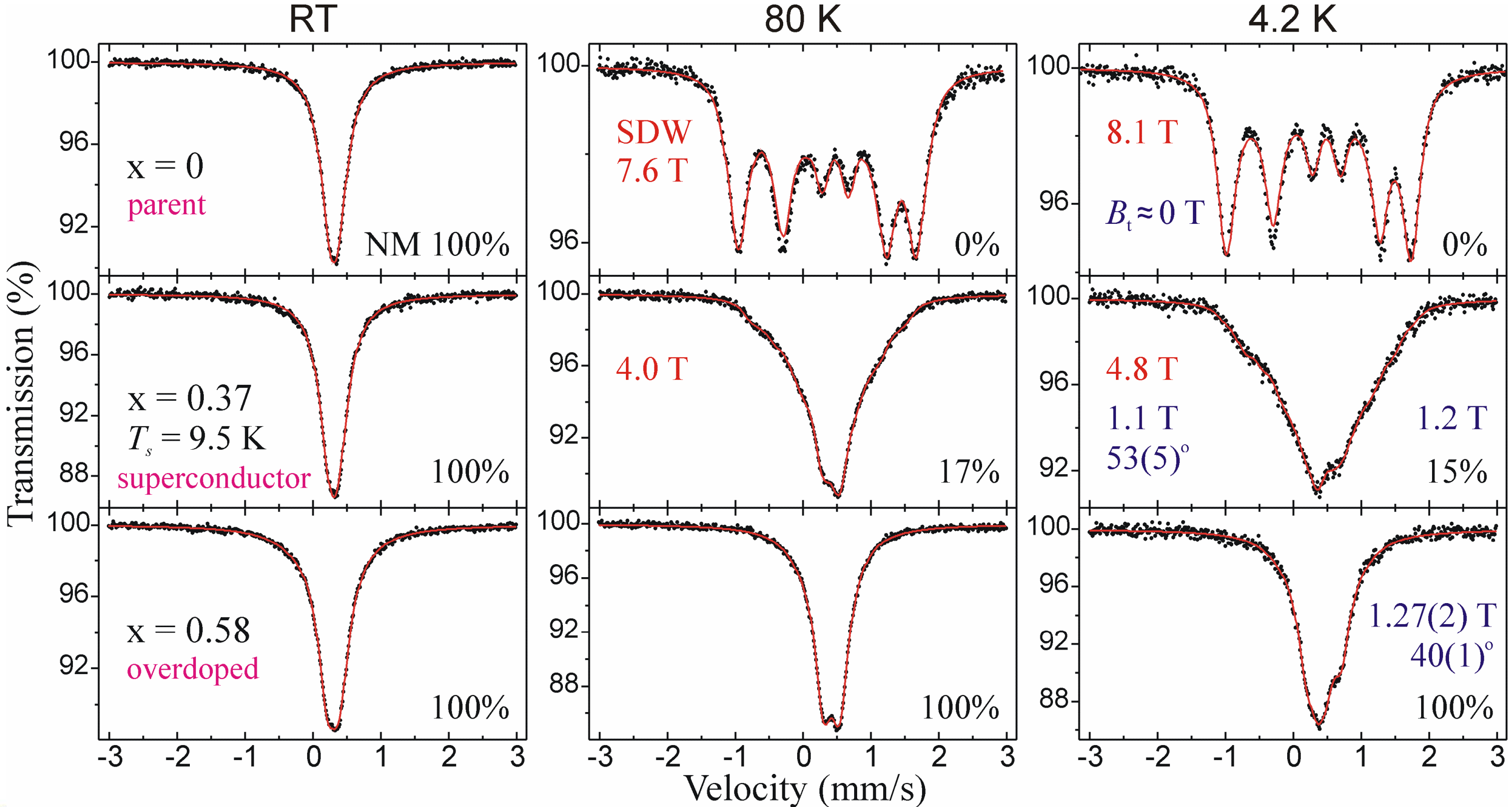
Eu^{2+} moments rotate from a-axis to c-axis.

Eu^{2+} magnetism and superconductivity coexist.

$EuFe_{2-x}Co_xAs_2$

^{57}Fe Mössbauer spectra

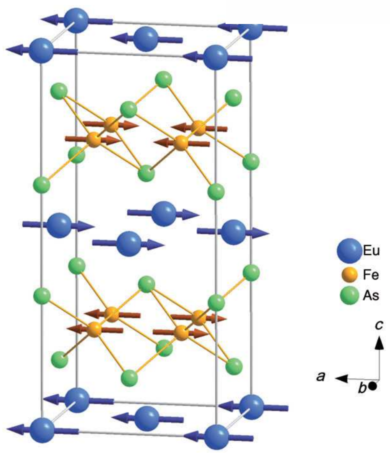
T_N (Eu) = 19 K

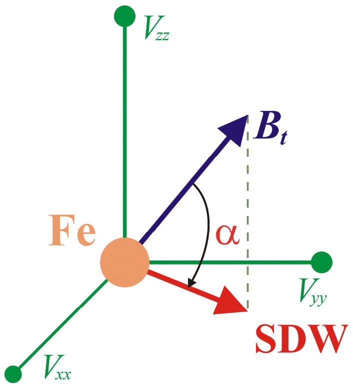


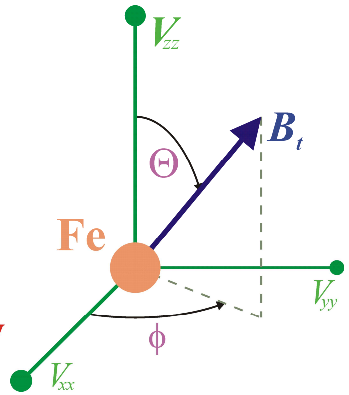
T_{SDW} = 190 K

T_{SDW} = 100 K

lack of SDW



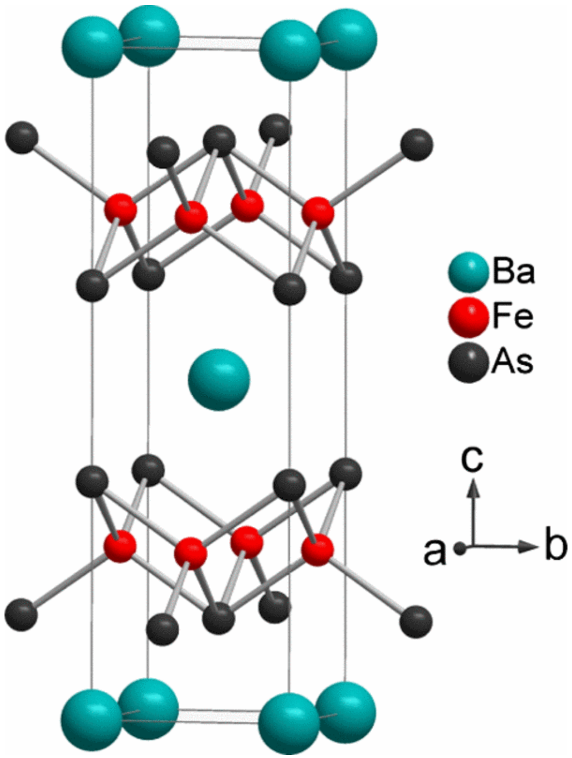


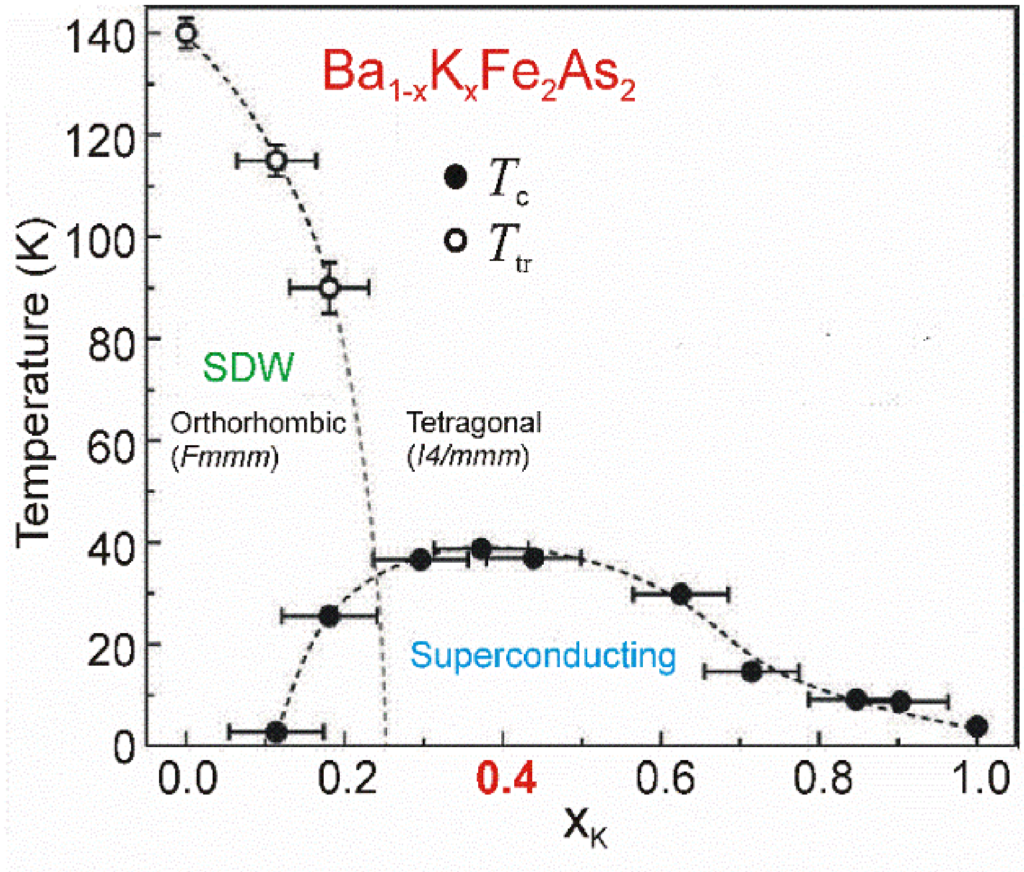


Eu^{2+} Transferred Field on ^{57}Fe

$Ba_{1-x}K_xFe_2As_2$

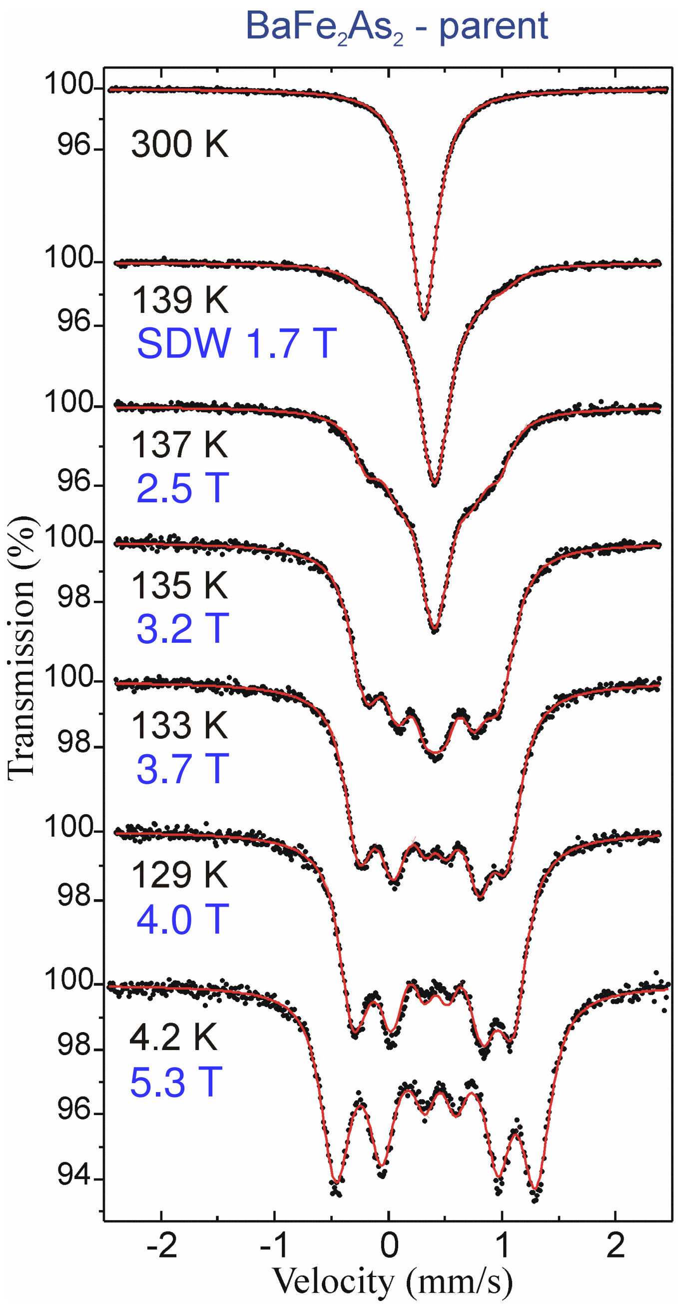
parent compound $BaFe_2As_2$ ⇨ doping K ⇨ superconductor $T_{sc} = 38K$

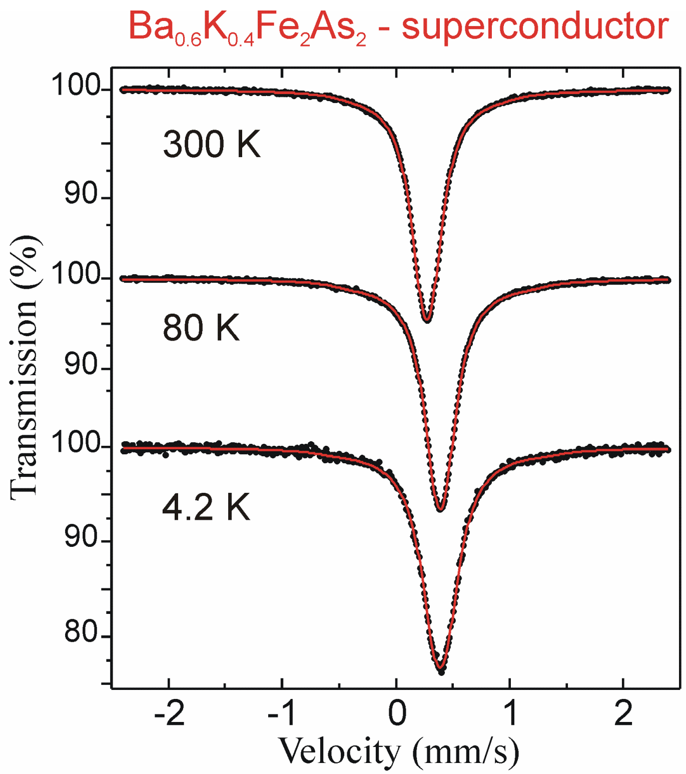


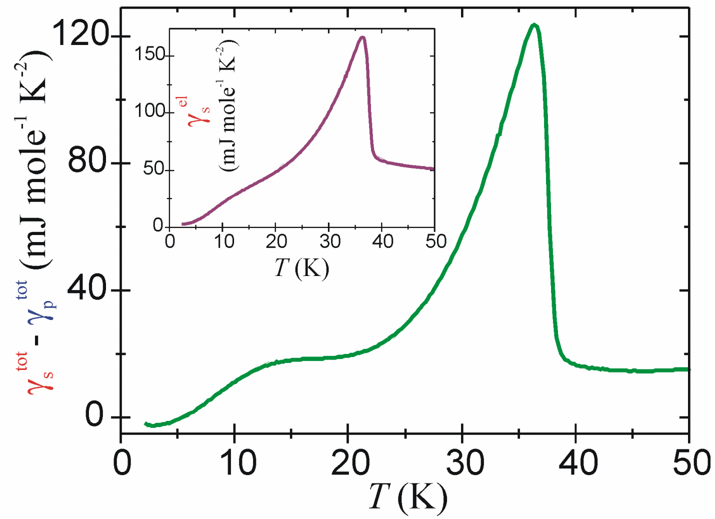


A.K.Jasek, K.Komędera, A.Błachowski, K.Ruebenbauer, Z.Bukowski, J.G.Storey, J.Karpinski,
Electric field gradient wave (EFGW) in iron-based superconductor $Ba_{0.6}K_{0.4}Fe_2As_2$ studied by Mössbauer spectroscopy,
J. Alloys Compd. **609**, 150 (2014)

^{57}Fe Mössbauer spectra of $BaFe_2As_2$ parent compound and $Ba_{0.6}K_{0.4}Fe_2As_2$ superconductor

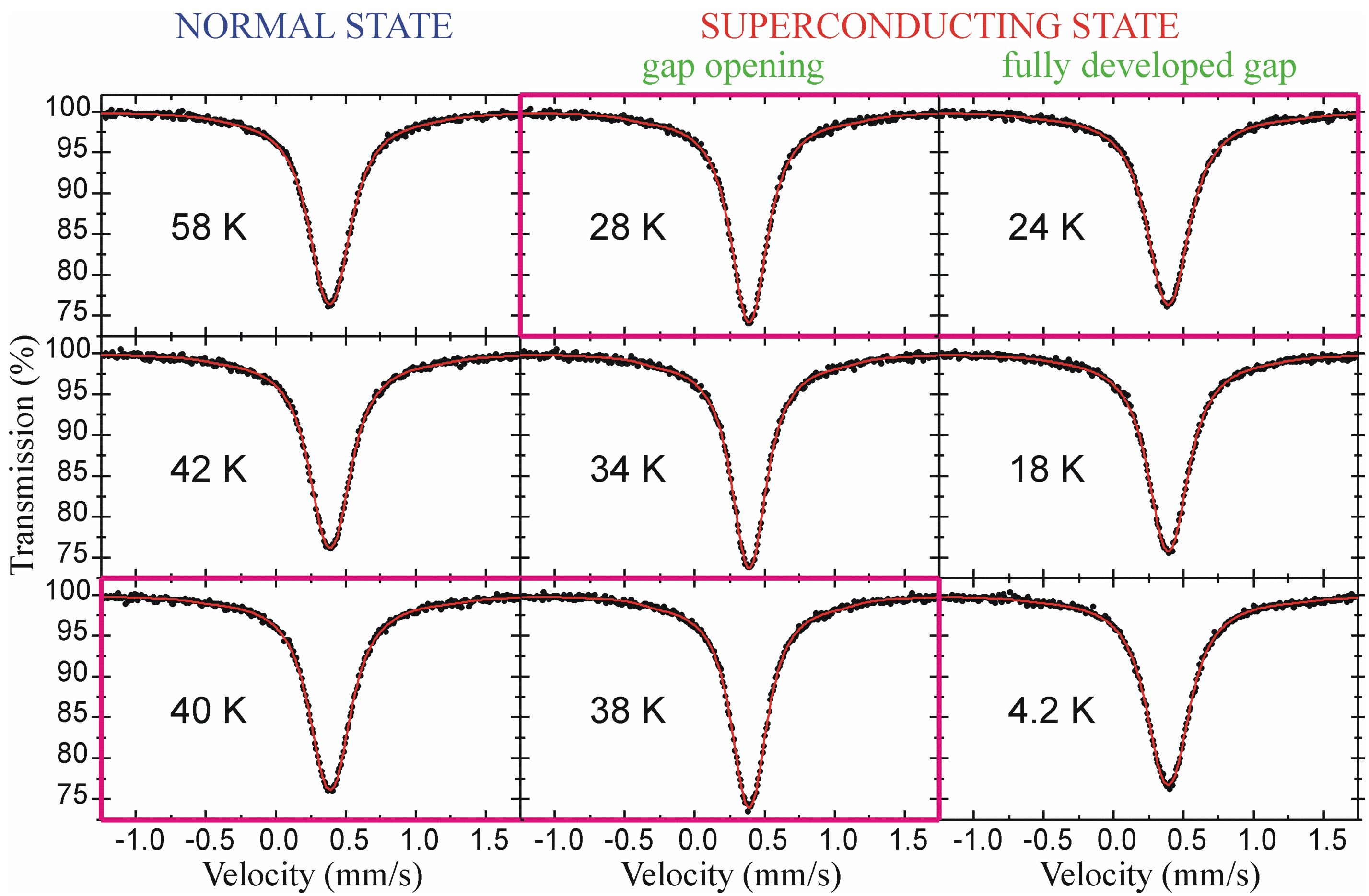


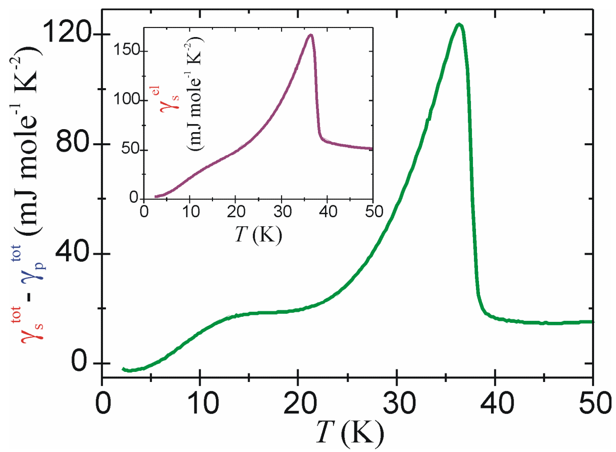




Difference in total molar specific heat coefficients between superconductor and parent compound.
Inset shows electronic specific heat coefficient of superconductor.

^{57}Fe Mössbauer spectra of the $\mathbf{Ba_{0.6}K_{0.4}Fe_2As_2}$ ($\boldsymbol{T_{SC}}$ **= 38 K)** across transition to the superconducting state.





Difference in total molar specific heat coefficients between superconductor and parent compound.
Inset shows
electronic specific heat coefficient of superconductor.

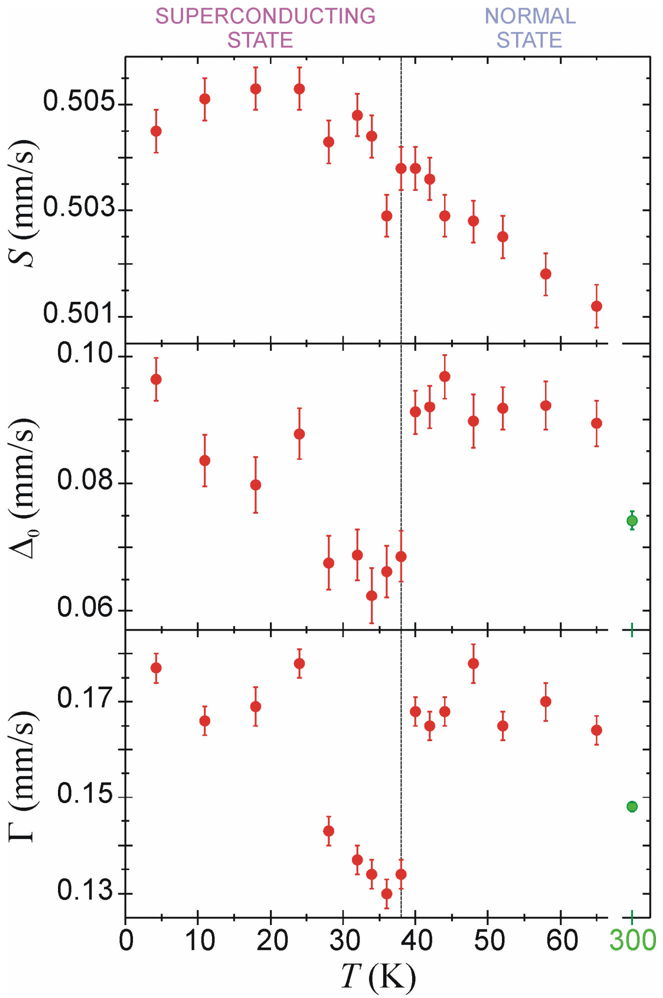
$Ba_{0.6}K_{0.4}Fe_2As_2$ (T_{SC} = 38 K)

Mössbauer parameters:

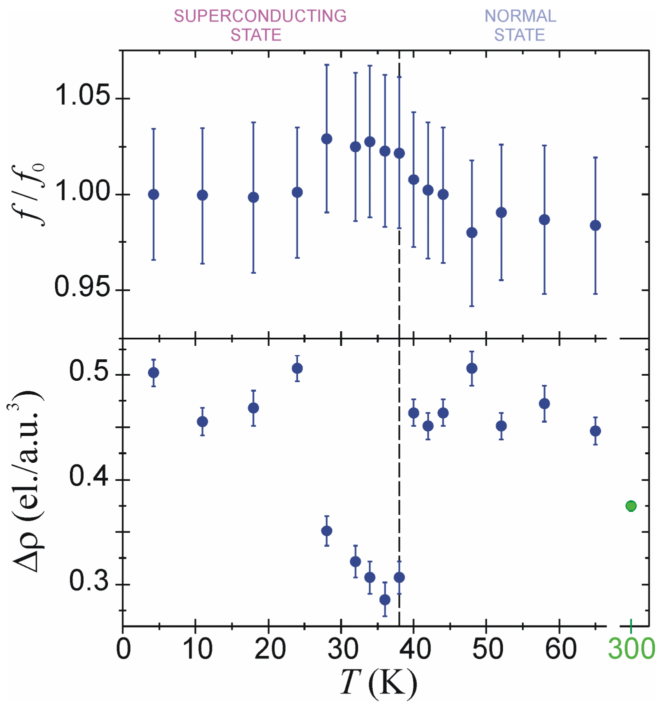
S – spectrum shift versus α-Fe

Δ_0 – constant component of quadrupole splitting

Γ – absorber line width

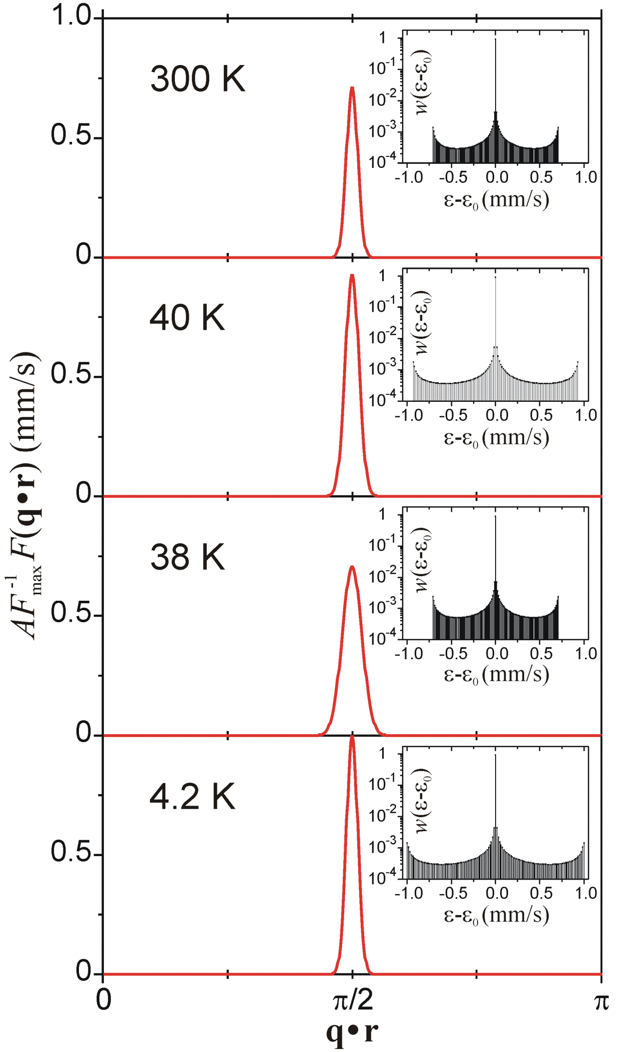


Relative recoilless fraction f/f_0
(normalized to f_0 at 4.2 K)



Dispersion of **CDW**
charge density wave
(**s** electrons density variation)

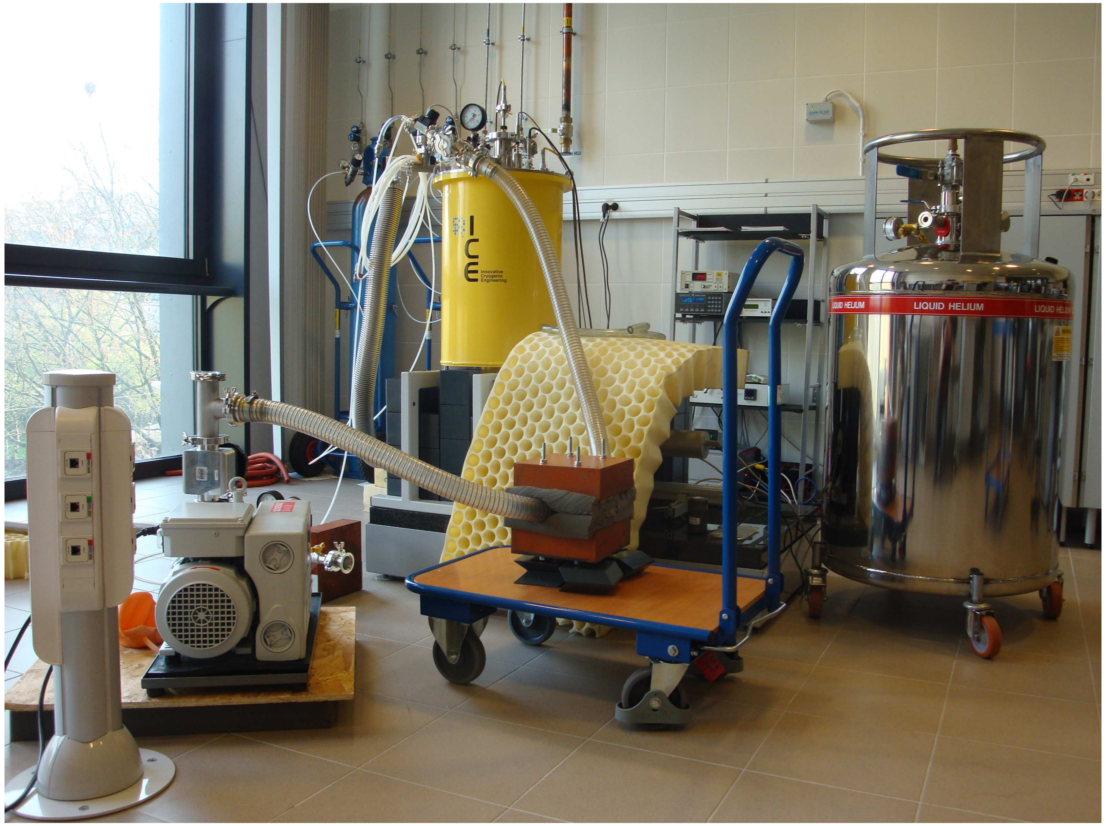
Shape of **EFGW**
electric field gradient wave
(**d** electrons density variation)

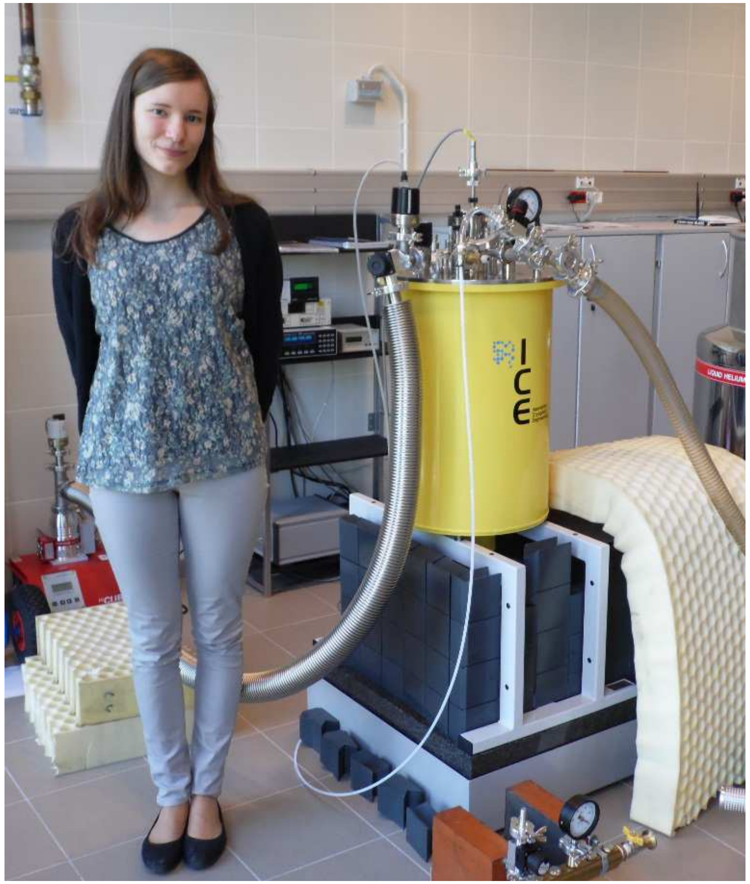


EFG

1 mm/s → 5.7 ·10^{21} V/m^2

Laboratorium Spektroskopii Mössbauerowskiej
Akademickie Centrum Materiałów i Nanotechnologii AGH





Magdalena Piskorz
WFiIS AGH, Fizyka Techniczna, III rok

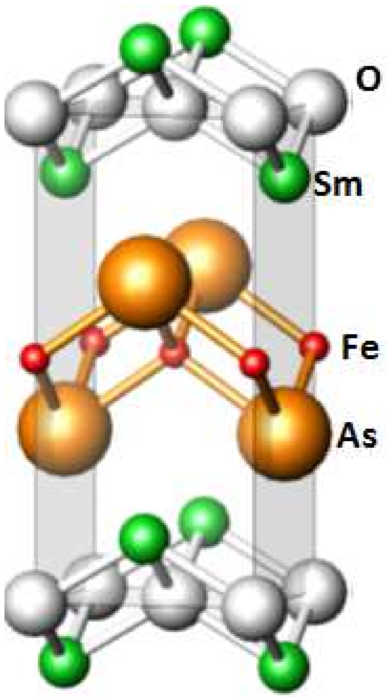
Czułość spektroskopii mössbauerowskiej na przejścia nadprzewodzące w pniktydkach żelaza

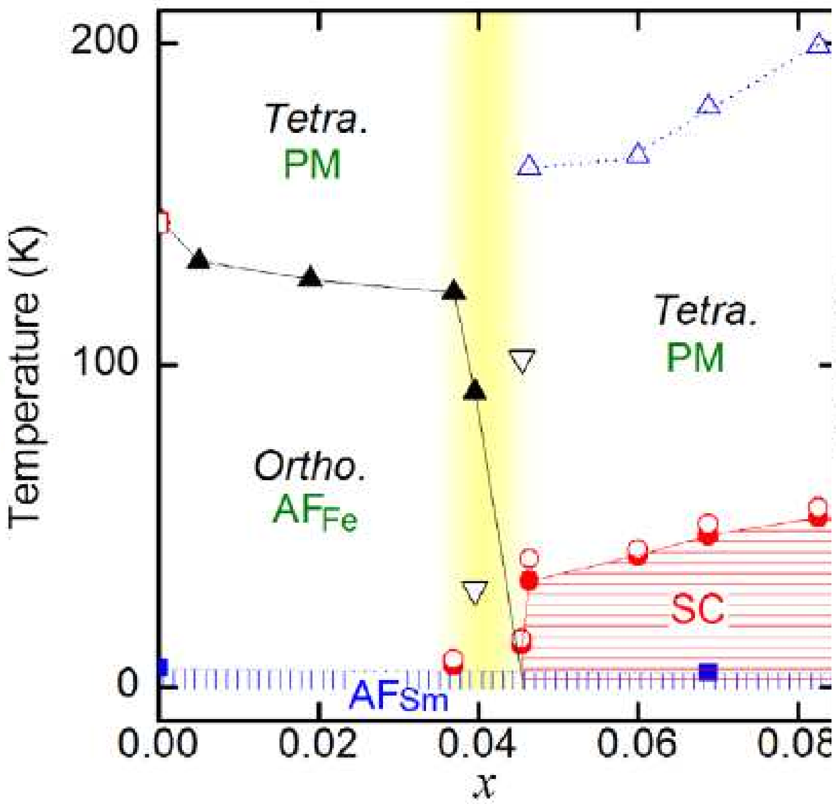
51 Konferencja Studenckich Kół Naukowych AGH
maj 2014
WYRÓŻNIENIE

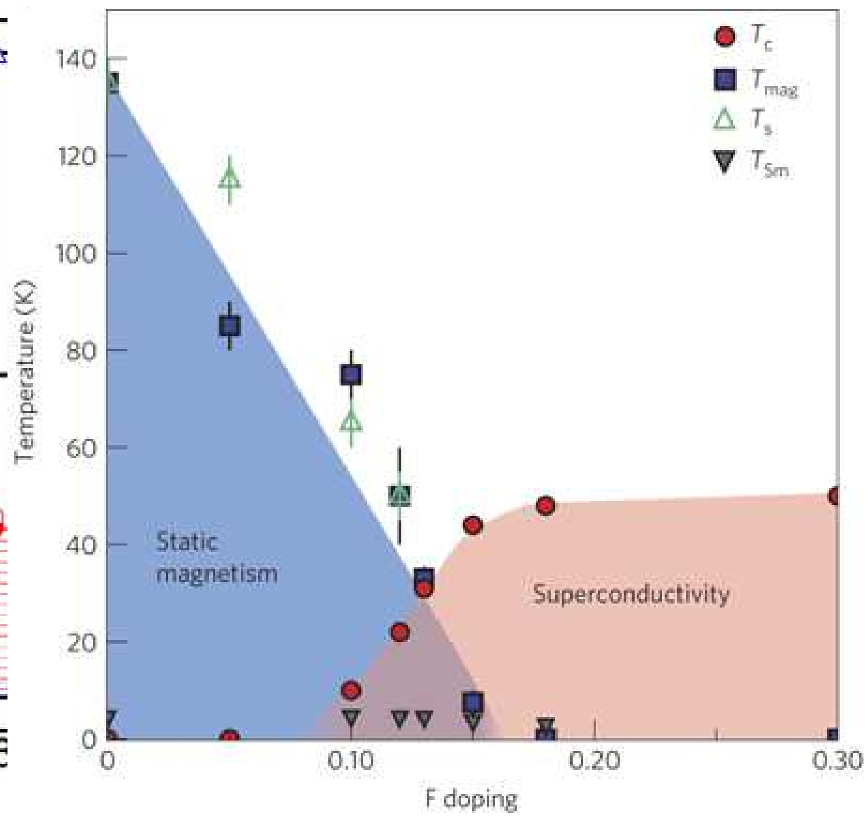
$SmFeAsO_{1-x}F_x$

parent compound → doping → superconductivity

SmFeAsO → F → T_{sc} = 55K







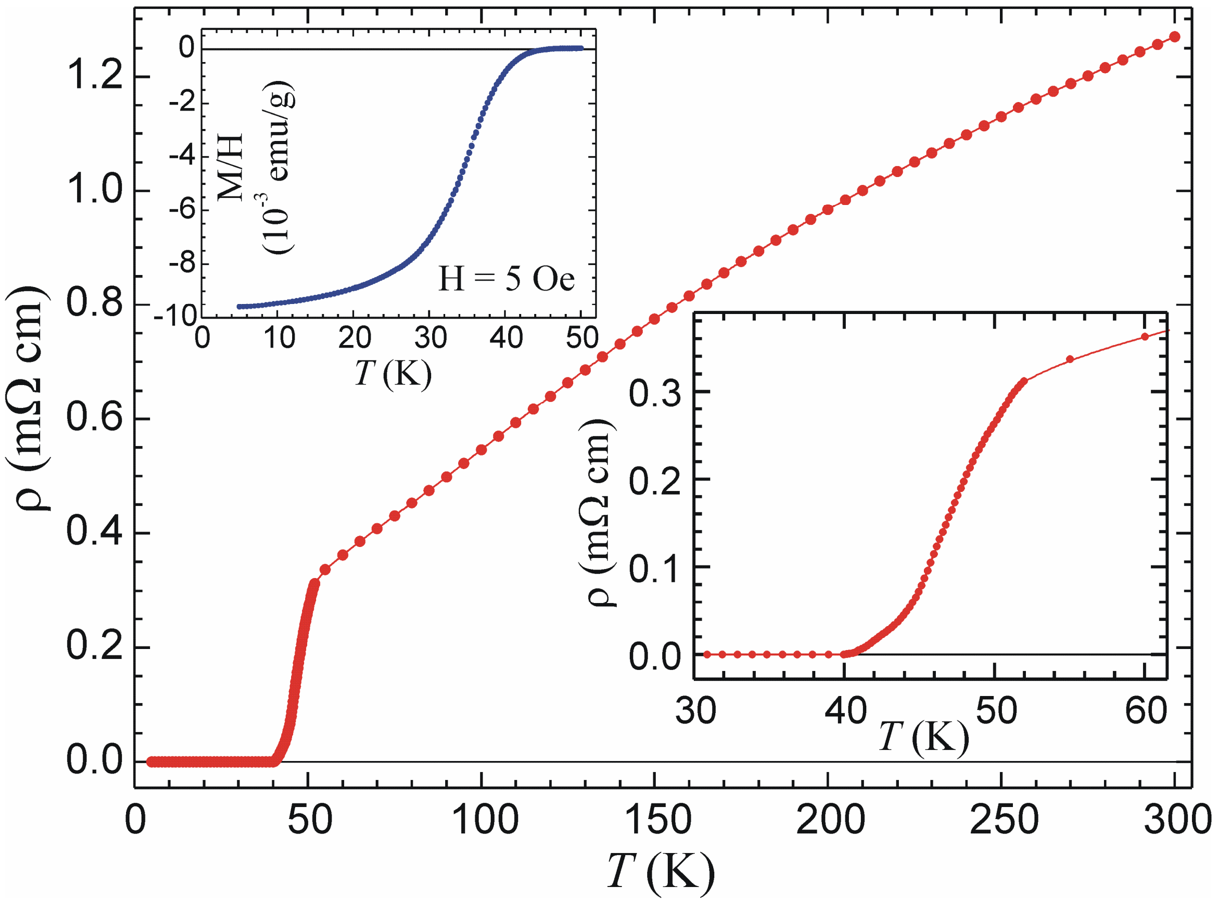
Y. Kamihara *et al.*, New J. Phys. **12**, 033005 (2010)   A.J. Drew *et al.*, Nature Materials **8**, 310 (2009)

our sample – **$SmFeAsO_{0.91}F_{0.09}$**

$SmFeAsO_{0.91}F_{0.09}$

Resistivity and magnetic susceptibility

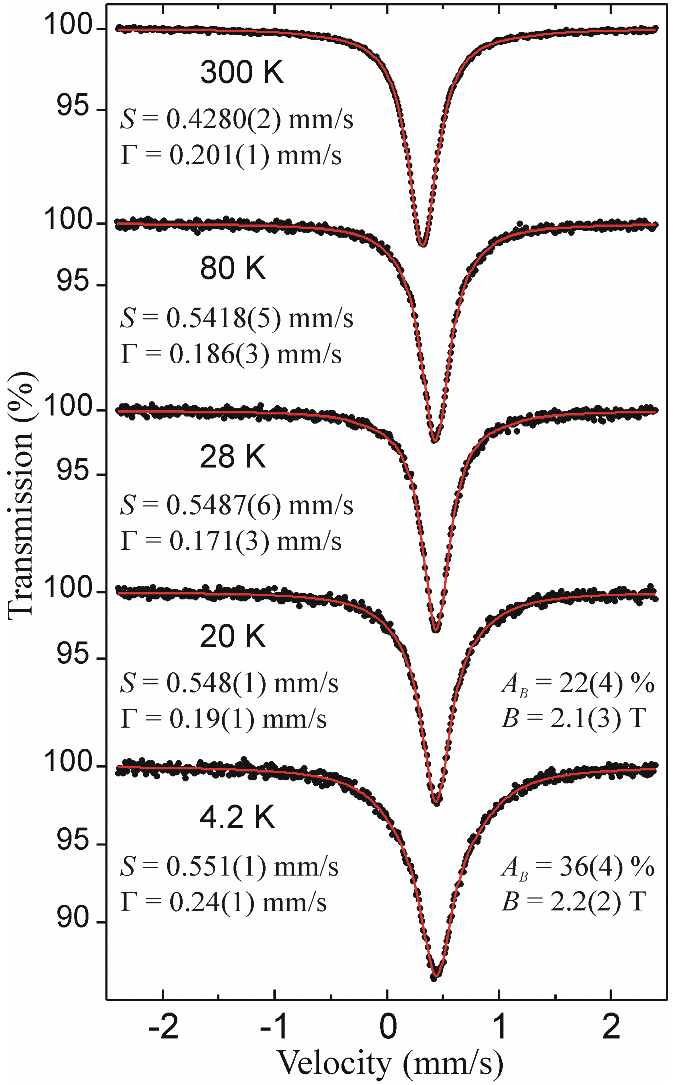
$T_{sc} \approx 47$ K



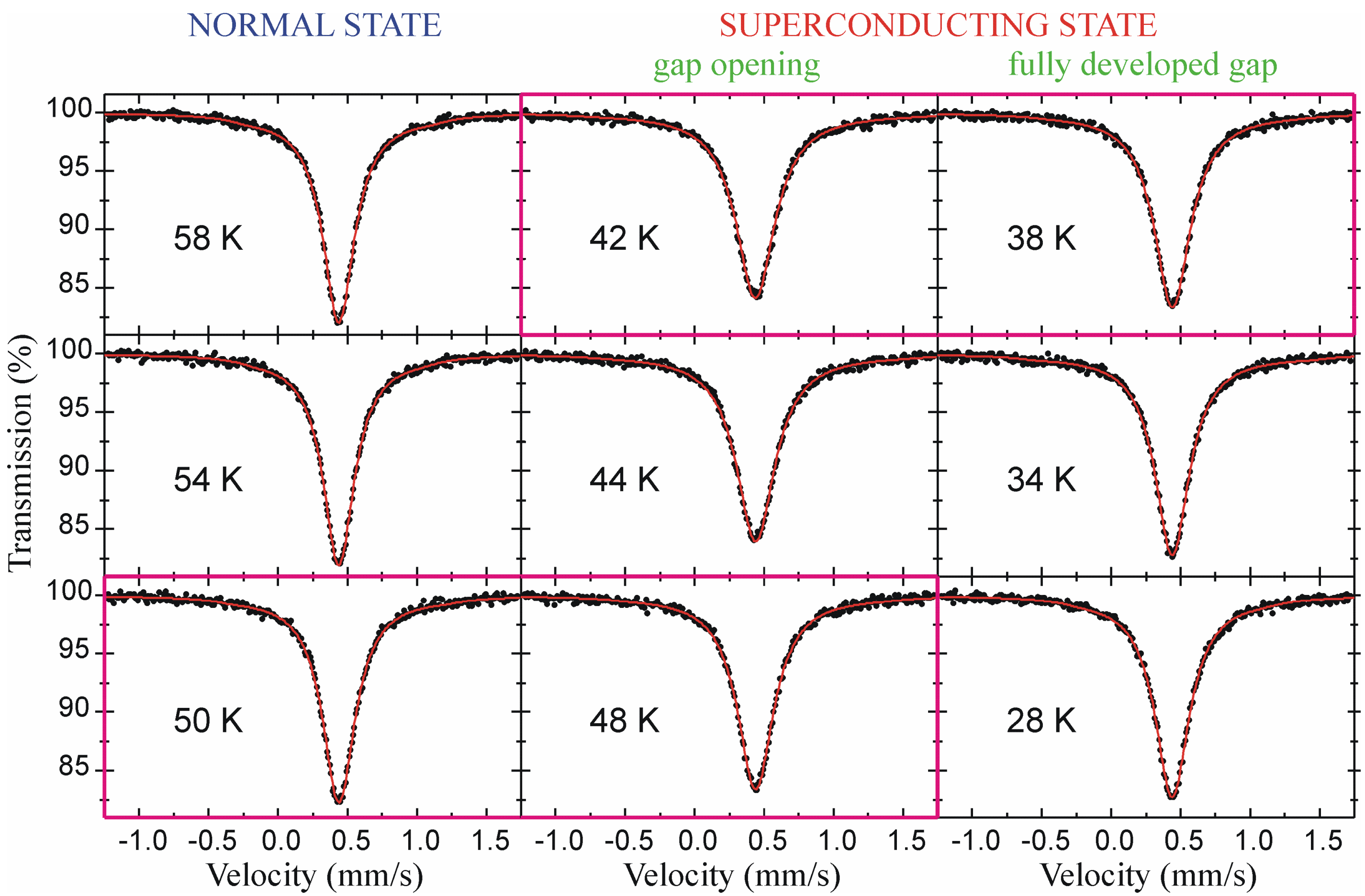
A.K.Jasek, K.Komędera, A.Błachowski, K.Ruebenbauer, H.Lochmajer, N.D.Zhigadlo, and K.Rogacki,
J. Alloys Compd. **658**, 520 (2016)

^{57}Fe Mössbauer spectroscopy

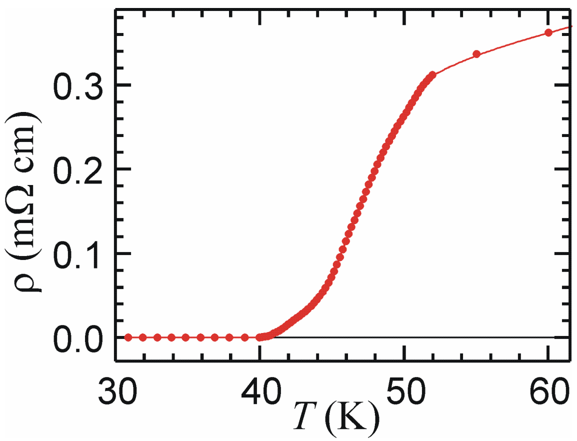
magnetic spectral broadening below ***28 K***

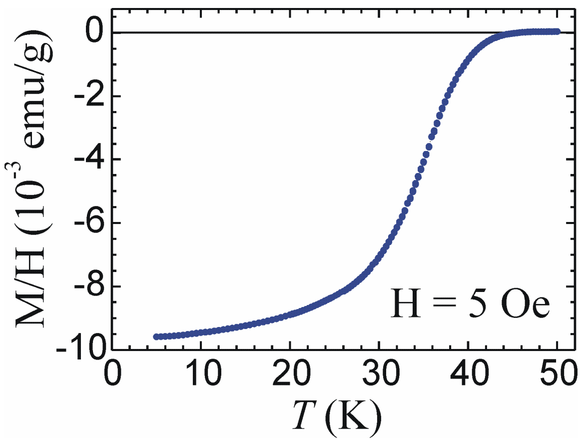


^{57}Fe Mössbauer spectra of **$SmFeAsO_{0.91}F_{0.09}$** (**T_{sc} ≈ 47 K**) across transition to the superconducting state



Resistivity

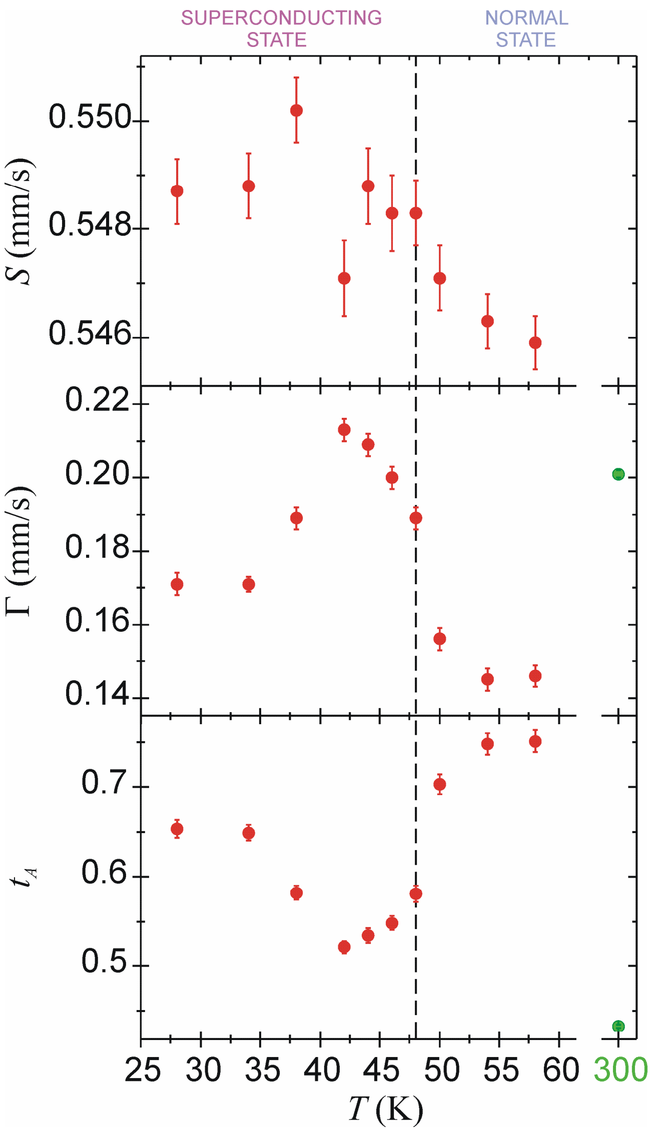




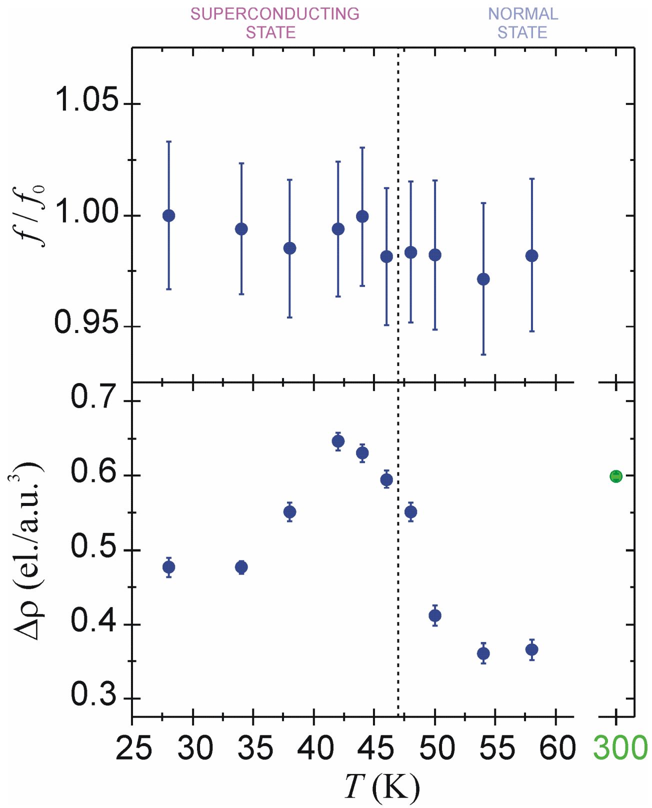
Magnetic susceptibility

$SmFeAsO_{0.91}F_{0.09}$
($T_{sc} \approx 47$ K)

Mössbauer spectra parameters



Relative recoilless fraction f/f_0 (normalized to f_0 at 28 K)



Dispersion of **CDW**

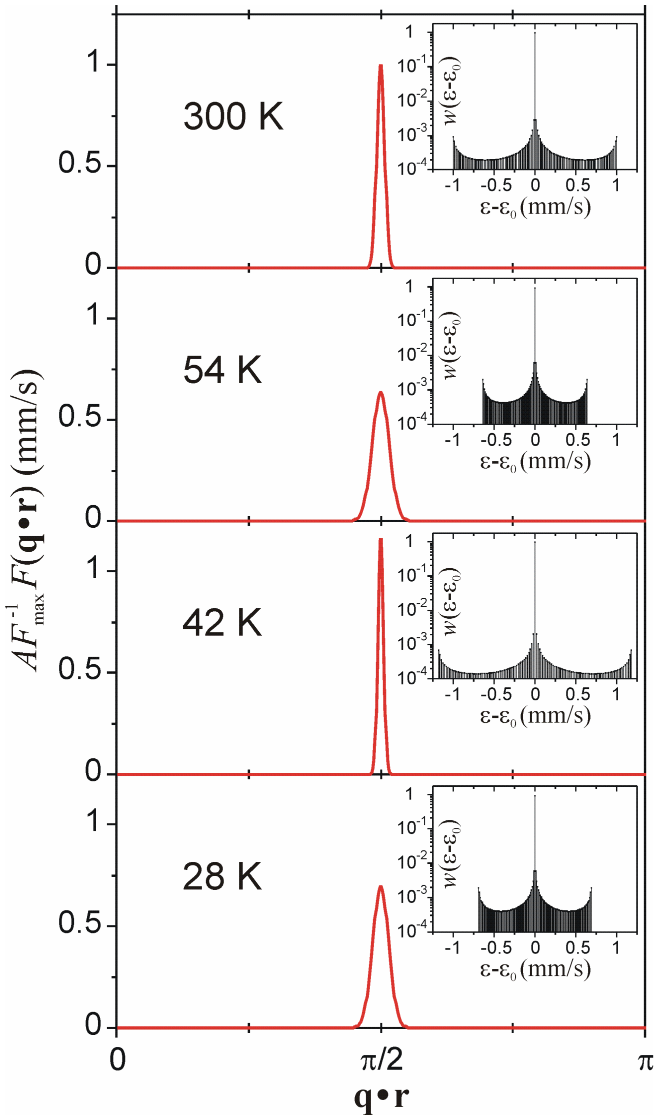
charge density wave

(**s** electrons density variation)

Shape of **EFGW**

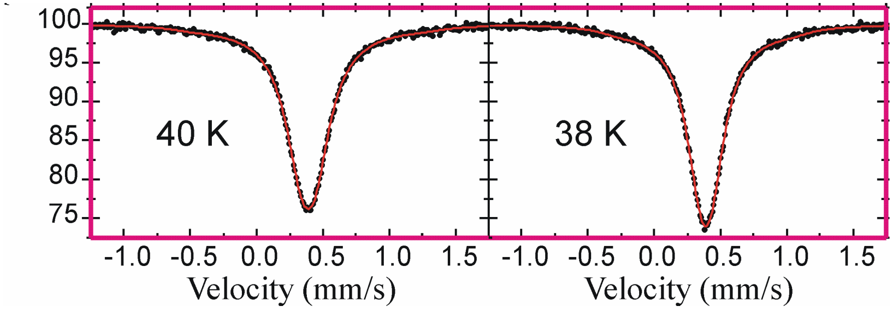
electric field gradient wave

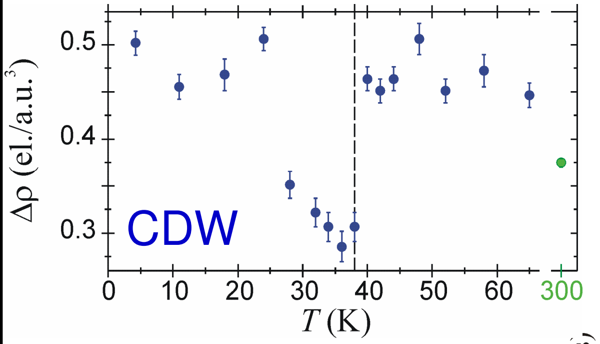
(**d** electrons density variation)

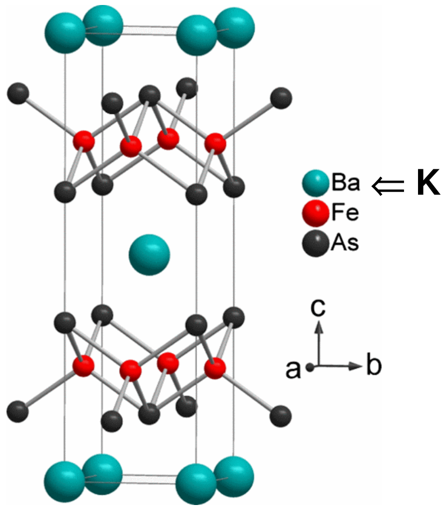


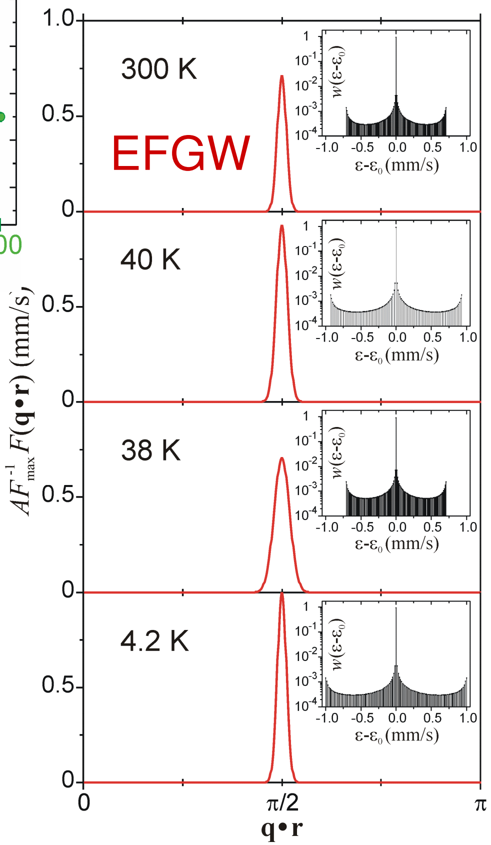
Comparison between charge density modulation changes during superconducting transition in

$Ba_{0.6}K_{0.4}Fe_2As_2$ T_{sc} = 38 K (hole doping)

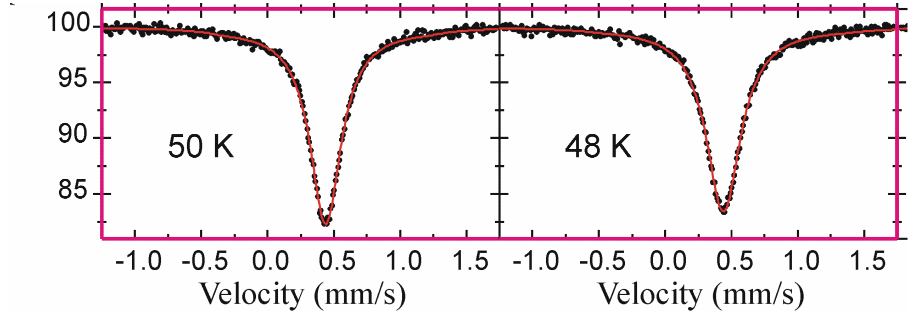


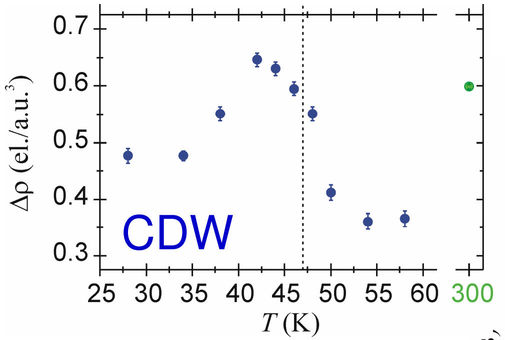


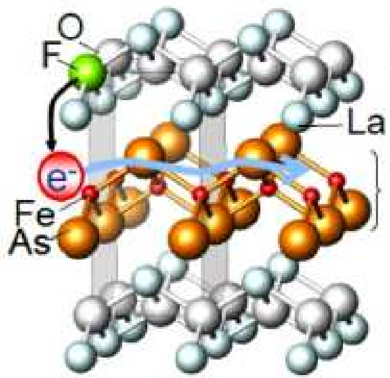


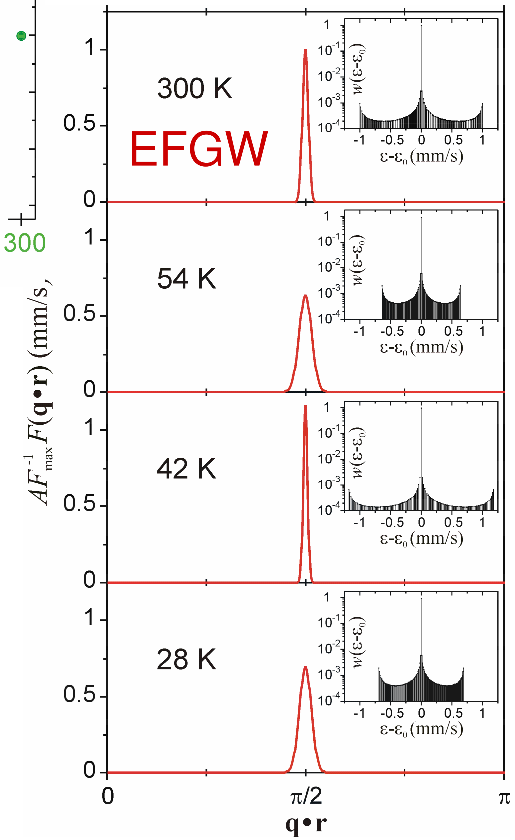


$SmFeAsO_{0.91}F_{0.09}$ T_{sc} = 47 K (electron doping)



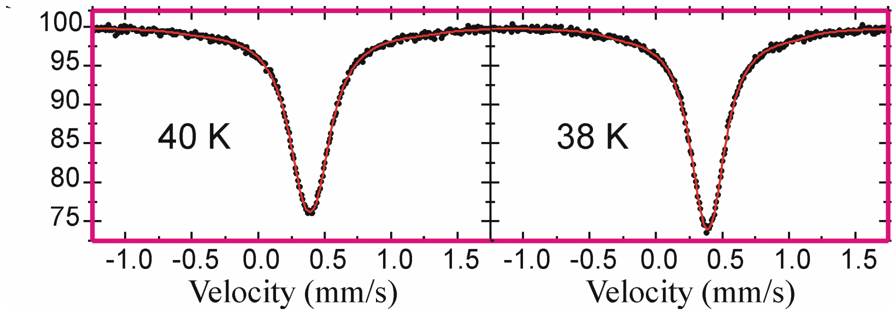


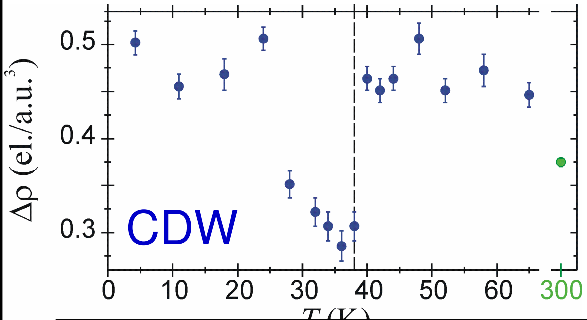


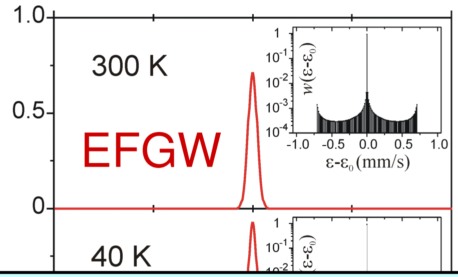


Comparison between
charge density modulation changes during superconducting transition in

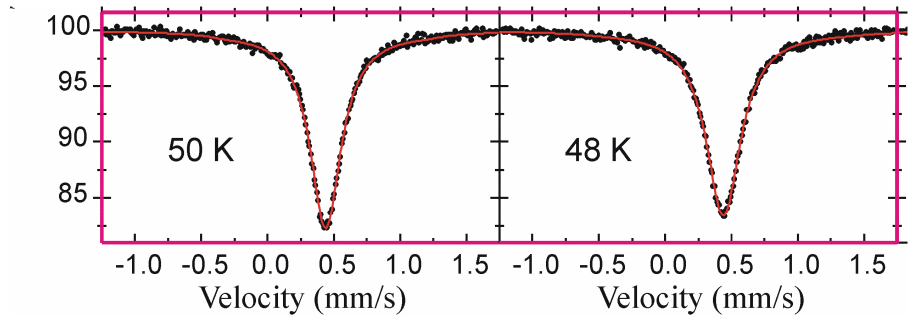
$Ba_{0.6}K_{0.4}Fe_2As_2$ T_{sc} = 38 K
(hole doping)

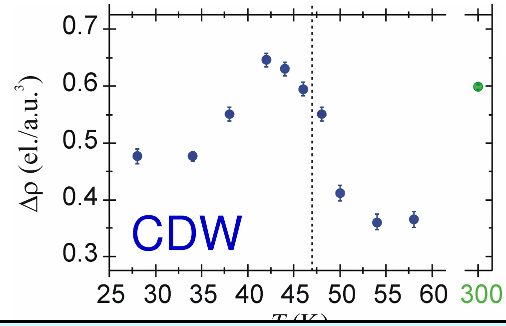


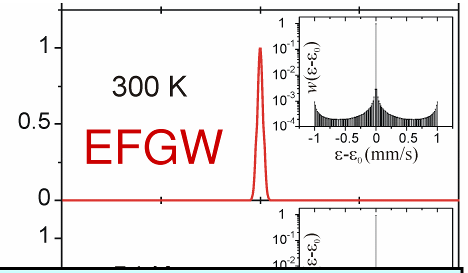




$SmFeAsO_{0.91}F_{0.09}$ T_{sc} = 47 K
(electron doping)



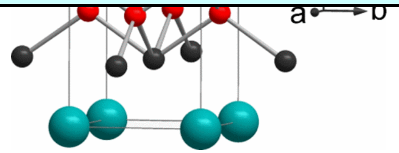


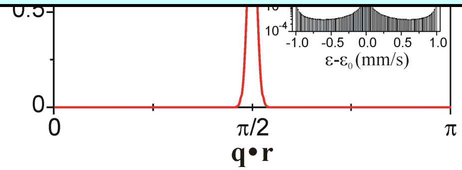


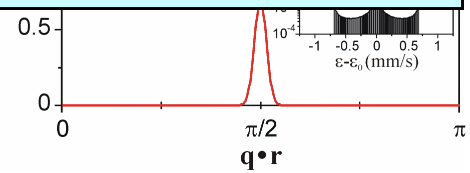
1) Mössbauer spectroscopy sees CDW in Fe-SC.

2) CDW modulation is perturbed at T_{sc}-onset and returns to the modulation from the normal state below T_{sc}-offset (ρ=0).

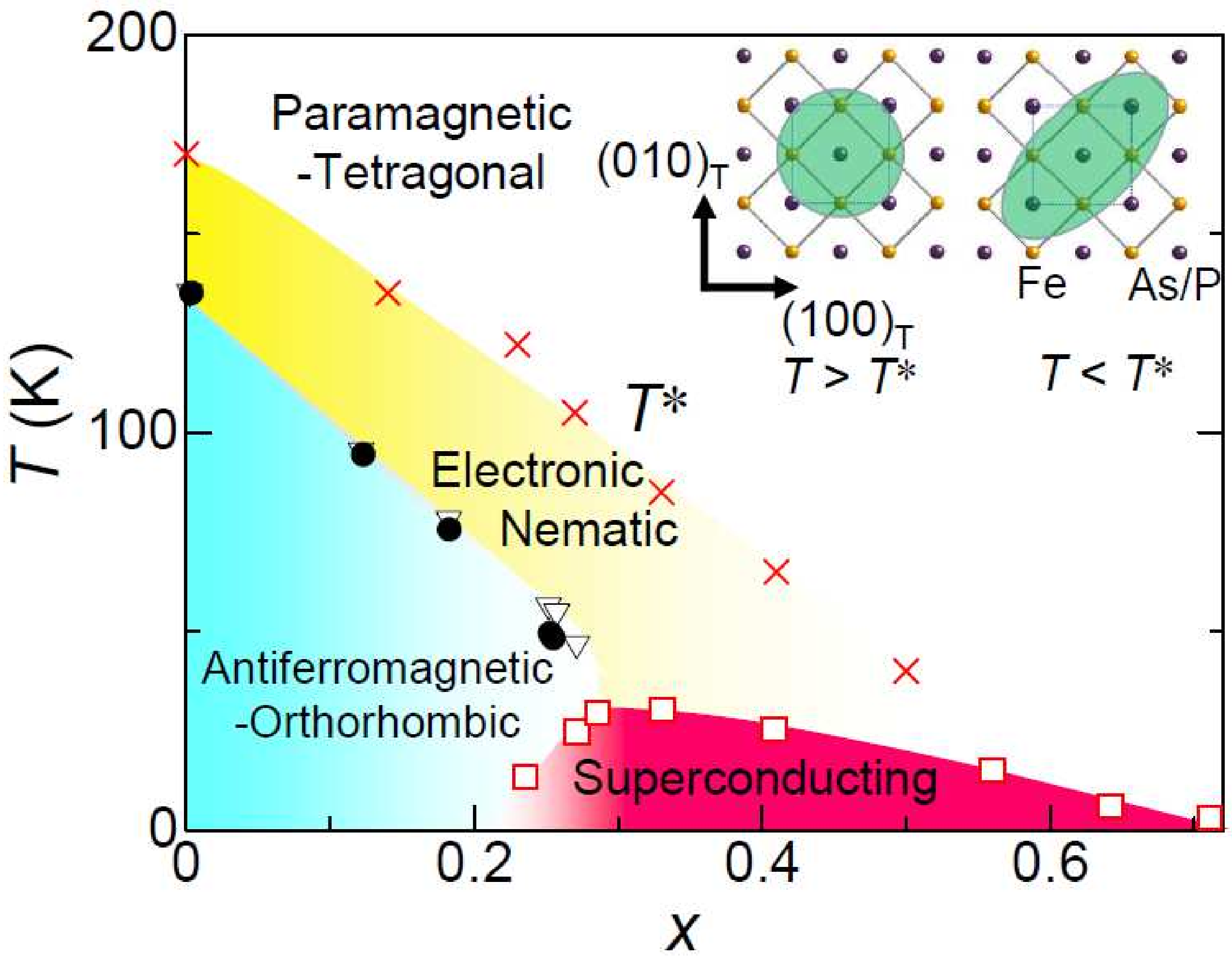
3) Direction of CDW perturbation depends on … *type of doping (?)*







$BaFe_2(As_{1-x}P_x)_2$



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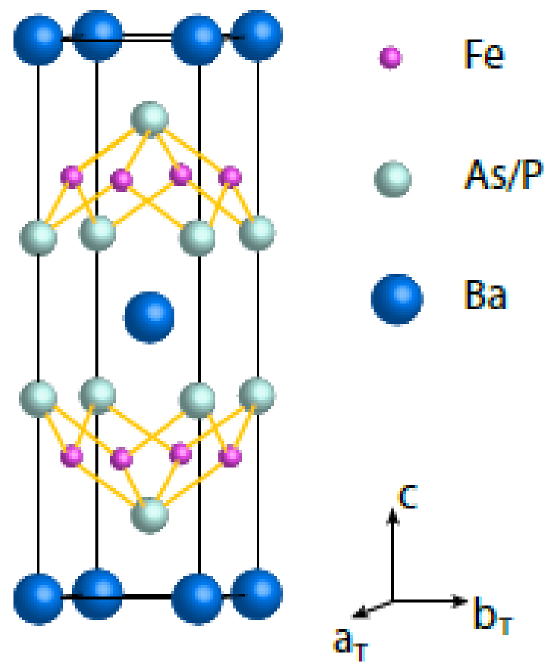
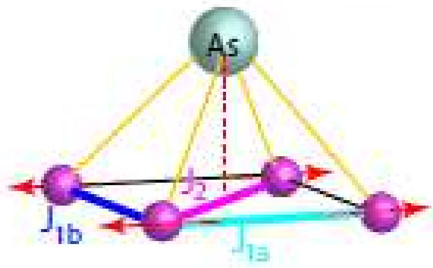
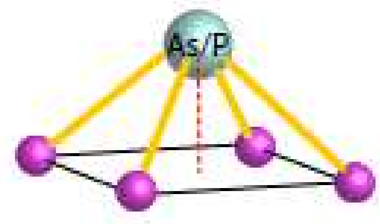


x = 0 **h_{Pn} = 1.36 Å**

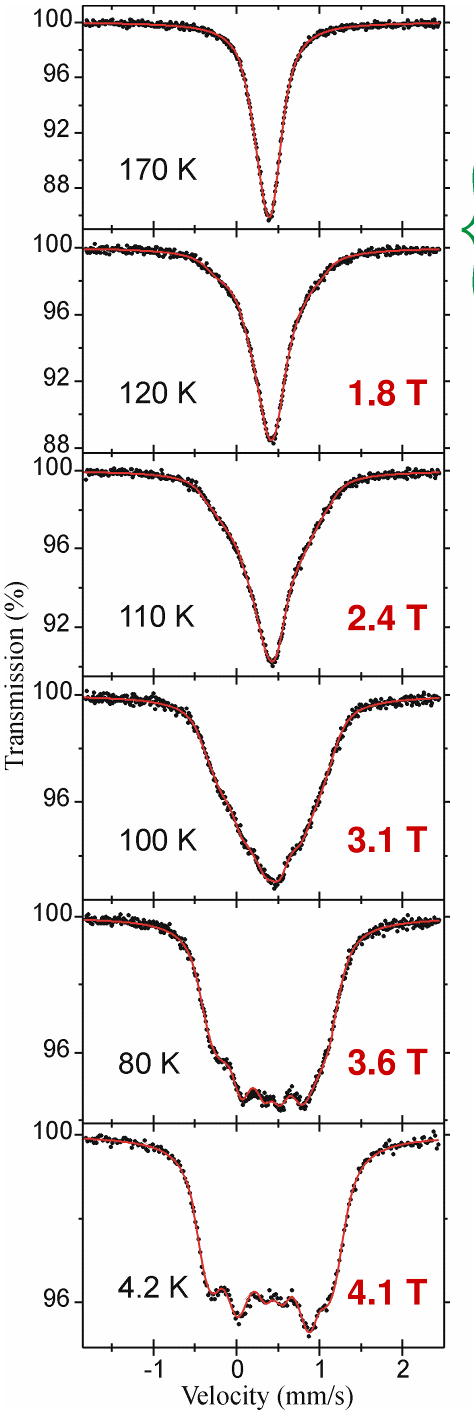


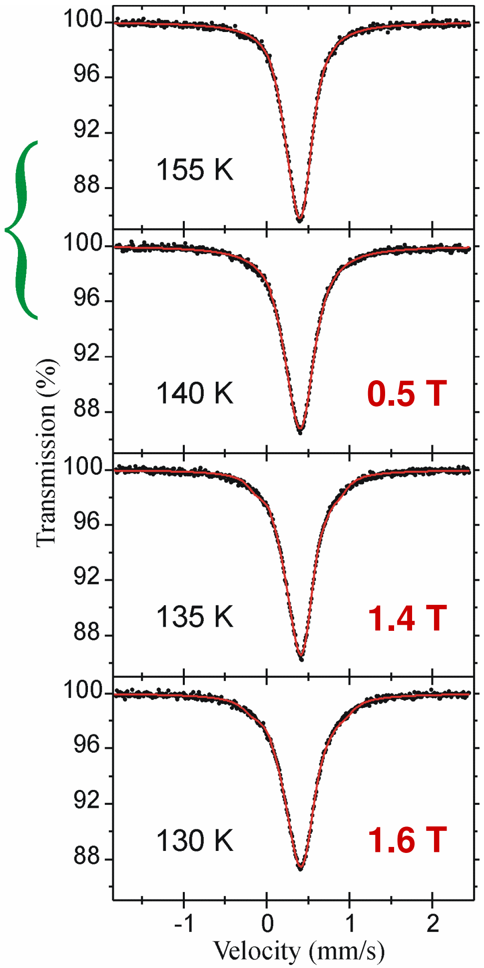
x = 0.30 **h_{Pn} = 1.28 Å**

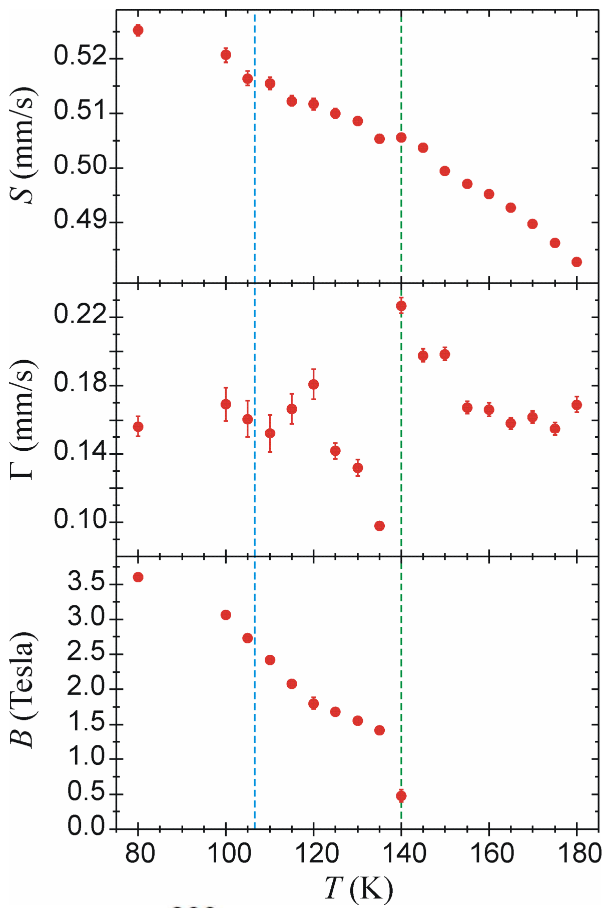


<u>Nematic phase</u> is characterized by electronic anisotropy in *a-b* plane
with broken rotational symmetry
but preserved translational symmetry (tetragonal phase).

$BaFe_2(As_{1-x}P_x)_2$ **x = 0.10** T_{SDW} = 106 K





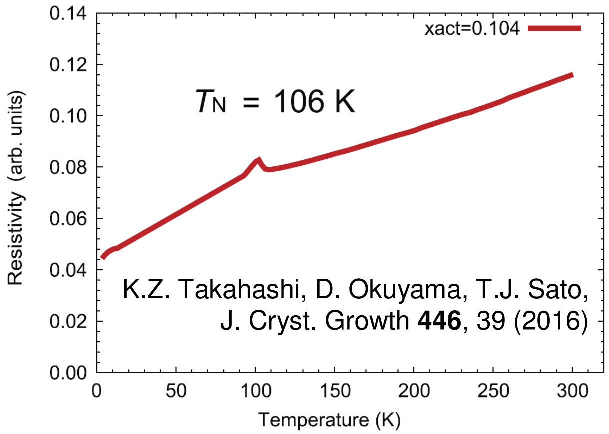


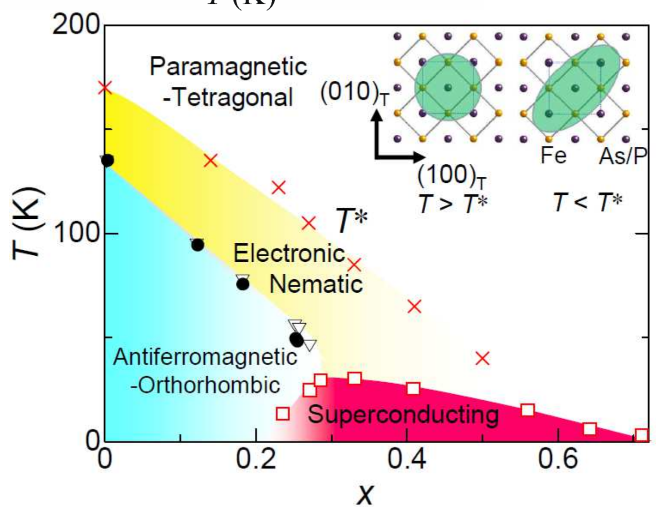
Mössbauer parameters:

S spectrum shift

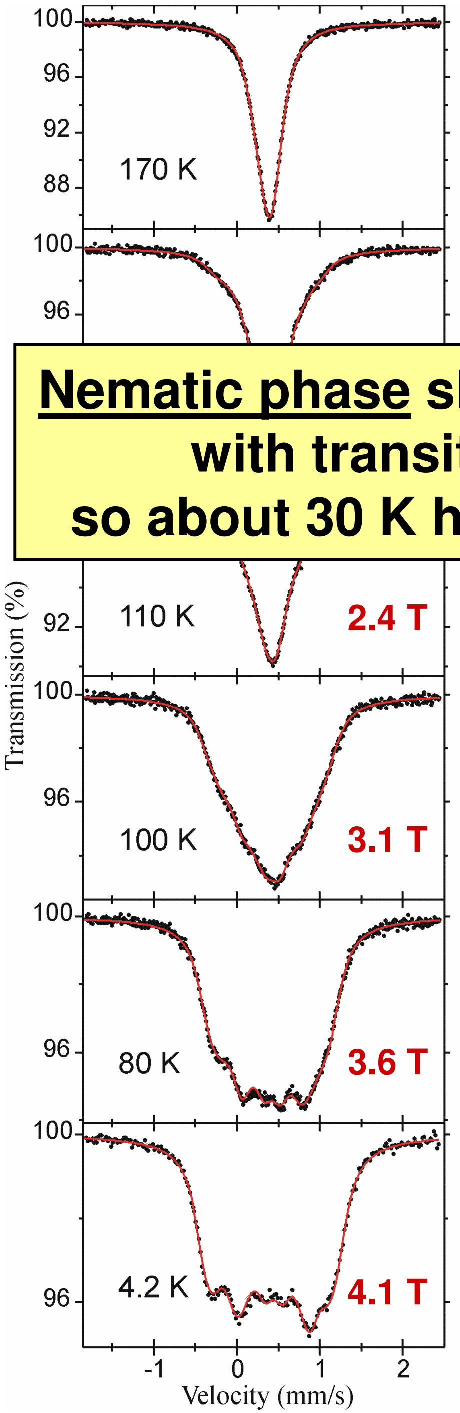
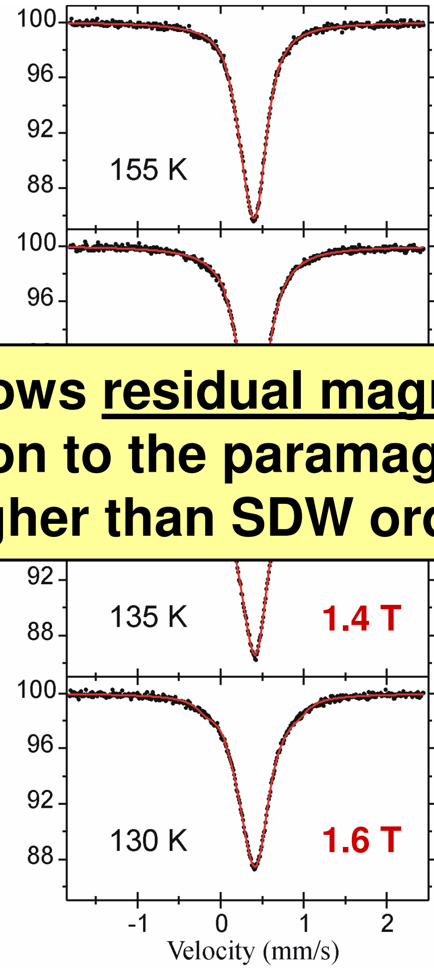
Γ line width

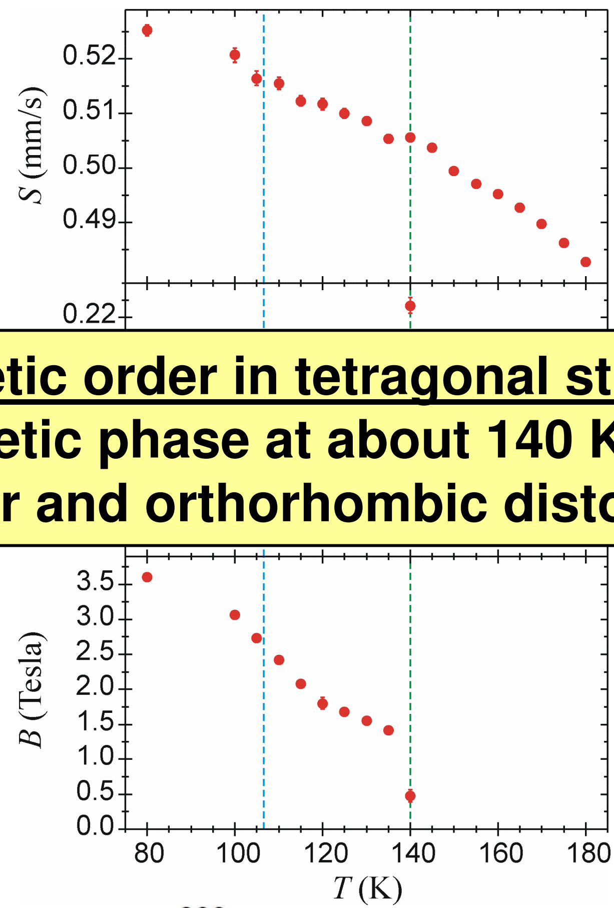
B **magnetic hyperfine field**





$BaFe_2(As_{1-x}P_x)_2$ **x = 0.10** T_{SDW} = 106 K

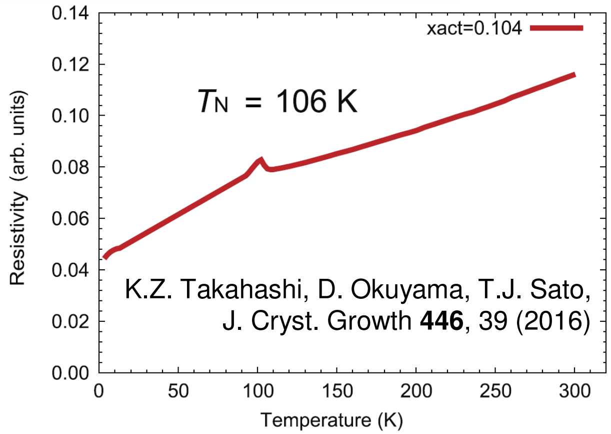


Mössbauer parameters:
S
spectrum shift

...dth

B
magnetic hyperfine field

Nematic phase shows residual magnetic order in tetragonal structure with transition to the paramagnetic phase at about 140 K, so about 30 K higher than SDW order and orthorhombic distortion.



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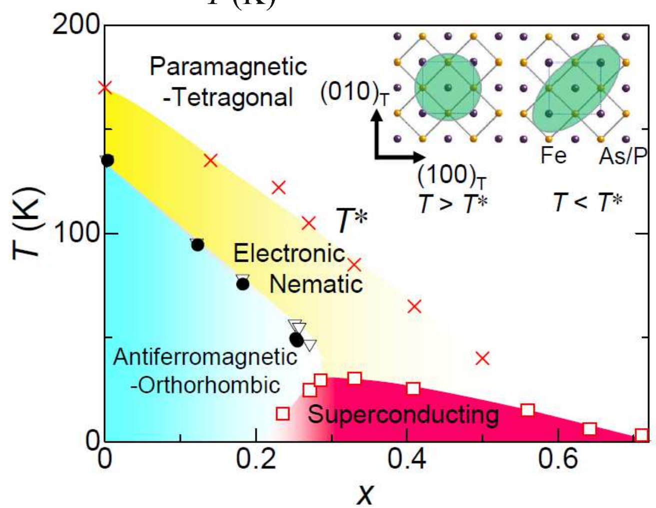

Conclusions

Precursor compound: **FeAs**

Antiferromagnetic incommensurate spirals propagate along c-axis with the hyperfine field varying along the spiral in a fashion resembling symmetry of 3d electrons (local magnetic moment) in a–b plane with significant distortion caused by arsenic bonding p electrons.

Parent compounds: **AFe_2As_2**

Longitudinal spin density wave SDW develops with triangular shape along propagation direction, i.e. a-axis. Upon temperature lowering they transform into rectangular form. Hence, they are indistinguishable from simple anti-ferromagnetic ordering close to the ground state.

Superconductors: **$Ba_{1-x}K_xFe_2As_2$** and **$SmFeAsO_{1-x}F_x$**

The Mössbauer spectroscopy is sensitive to the superconducting transition in Fe-based superconductors via **change of the electron charge density modulation**, which is seen via dispersion of isomer shift (CDW caused by s electrons) and via distribution of electric field gradient (EFGW caused by d electrons).

Shape and amplitude of EFGW and CDW are strongly perturbed at the superconducting transition. Namely, all modulations are strongly changed at critical temperature due to the superconducting gap opening and subsequent formation of Cooper pairs. However dispersion of the charge density and EFGW shape behave in the opposite ways for these two superconductors.

Thank you very much for your attention !